



Comparative study of site investigation approaches and potential in situ remediation techniques: model-assisted evaluation of advantages and uncertainties

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timbre

Tailored Improvement of
Brownfield Regeneration
in Europe

Comparative study of site investigation approaches and potential in situ remediation techniques: model-assisted evaluation of advantages and uncertainties

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Content

1. Introduction	4
2. Site characterization	9
2.1 Methods	9
2.1.1 Tree coring	10
2.1.2 Soil gas measurement	10
2.1.3 MIP/LIF/HPT/CPT/EC	11
2.1.4 Leaching tests for soil characterization	12
2.2 Test sites and application	13
2.3 Results	15
2.3.1 Hunedoara	15
2.3.2 Szprotawa	22
3. Site remediation	27
3.1 Methods	28
3.1.1 Soil washing	28
3.1.2 Phytoremediation	32
3.2 Results	37
3.2.1 Soil washing	37
3.2.2 Phytoremediation	40
3.3 Additional options	41
3.3.1 In-situ biological treatment with oxygen-enriched water and coupled vapour..... extraction: Szprotawa case	41
3.3.2 ISCO & Biological remediation: Szprotawa case	44
3.3.3 Combination of soil-flushing and air-sparging at Szprotawa site	46
4. Comparative evaluation of advantages and uncertainties	48
4.1 Investigation	48
4.2 Remediation	49
4.3 Short exemplary evaluation of remediation options for Szprotawa site	53
5. References	55
Annex I: Contributors to the report and Disclaimer	61
Contributors	61
Disclaimer	61

1. Introduction

The Timbre project aims at overcoming existing barriers to brownfield regeneration by developing and providing customised problem- and target-oriented packages of approaches, technologies and tools. As a unique asset, these packages deliberately include the cultural and administrative characteristics of the affected regions and their regional distinctive features. By providing a customisable toolbox, which specifically addresses the diverse processes that have to be dealt with during the course of a regeneration project, Timbre seeks to enable end-users to find best practice based solutions. The project's objective is to deliver a tailored training and dissemination programme as part of an information centre that will transfer existing and emerging knowledge to the scientific community and end-users.

In Working Package 4 (WP4), strategies and technologies for integrated site characterisation and remediation are investigated. Brownfields are often characterised by extended areas being polluted in soil and groundwater. Rapid industrial development and changes in land use and ownership have frequently led to complex and irregular contamination patterns, where sufficient information on the situation of contamination is often lacking. This accounts in particular for sites with a complex and partly unknown history of land use, and for those sites being abandoned since long time periods.

It is generally accepted that traditional approaches for site investigation and remediation are either not reliable enough or not cost effective. In particular, sites with significant economic pressure for re-development require appropriate time-optimized land management strategies to accelerate the decision making processes. Current remediation options are usually limited to source containment, excavation and deposition of contaminated material, i.e. measures which are often prohibitively expensive or inefficient.

Alternative approaches would allow rapid delineation of subsurface contamination followed by a cost-effective *in situ* clean-up strategy. This may be achieved through integration of highly adaptive site investigation tools for source delineation and *in situ* remediation technologies, which are based upon a "just enough" approach. Some emerging technologies are available for this task, which however did not yet reach a wide-spread implementation. Rapid, cost-effective and reliable strategies and technologies are required for site investigation as well as monitoring of subsurface contamination and *in situ* remediation.

Site investigation traditionally relies on a predefined survey grid with nodes where soil boring/monitoring well and fixed-laboratory investigations are combined, in order to provide a knowledge status capable to enable remediation-related decisions. A major short-coming is the small number of boreholes and sampling points, hampering a reliable characterisation of the subsurface.

Direct-push (DP)-based technologies such as soil gas measurements or Membrane Interface Probe MIP, Laser-Induced Fluorescence LIF can be applied to overcome these shortcomings, enabling both screening and detail subsurface investigations in comparatively short time periods and at low expenses, and can be applied in an adaptive manner. These techniques are performed by pushing and hammering small diameter hollow steel rods into the ground to acquire high resolution depth profiles of different physical and chemical parameters.

Soil, soil gas and groundwater samples can be taken, and various sensors are available to be added to the DP equipment in order to obtain subsurface information at a high level of detail without the compulsory need for permanent monitoring devices. In areas being inaccessible for heavy equipment, shallow DP with small (including hand-driven) devices can be used for soil sampling and investigations in shallow aquifers (shallow soil probing, SSP). The application of DP-technology has strongly increased during the last years and became a viable alternative to conventional methods for site investigation (Dietrich and Leven 2006; ASTM 1998; U.S. EPA 1998; Jacobs et al. 2000; Pitkin et al. 1999). However, this technology is not implemented as a widely applied technology within Europe, yet.

Plants may also be used as a bioindicator of subsurface pollution, as many pollutants in the soil matrix are readily transferred into vegetation. Trees are to be preferred to smaller plants as their large root system can absorb chemicals from a larger area and greater soil depths. Wood and/or other plant parts are sampled for detection as well as for monitoring of soil and/or groundwater contamination and natural attenuation. The advantage of using wood from trees as a bio-indicator is that the method of tree coring is simple, easy, fast (60-80 trees/day) and inexpensive procedure which allows a high sampling density. As the relation between plant and soil/groundwater concentration is often non-linear, vegetation sampling is applied as a semi-quantitative methodology. Polar persistent chemicals are known to be well taken up from soil into roots and further translocated to stem and leaves (Trapp 2007, Dettenmaier et al. 2009). The uptake into plants for a range of compounds has been studied, such as cyanide (Larsen et al. 2005), iron cyanide (Larsen and Trapp 2006), phenol (Ucisik and Trapp 2006), dichlorophenol (Ucisik et al. 2007), selected heavy metals (Algreen et al. 2012, 2013), chloroethenes (Sorek et al. 2008, Larsen et al. 2008) and others. Phytoscreening, such as tree coring, is a promising low-invasive approach for obtaining information on a screening level covering extended contaminated sites.

A new concept using plants for screening and monitoring of subsurface contamination was developed and tested, in order to obtain information covering large contaminated sites. Different conditions of site characteristics and contamination (compounds) were considered. Tree coring were conducted complementarily and in parallel to direct push (DP) and shallow soil probing (SSP). Aims were to fill data gaps given by each method (some areas were not accessible for DP/SSP, others suffered from lack of vegetation) and furthermore to validate the methods and to test their feasibility. Parallel DP/SSP and plant investigations also aimed at gaining insight into plant uptake processes (such as relevant depths and spatial distribution of contaminants in the subsurface), which has rarely been investigated to date. New coupled strategies for adaptive site investigation and monitoring of subsurface pollution were developed, using direct-push (DP), shallow soil probing (SSP) and phytoscreening. Objectives were (i) site screening in order to obtain either first or complementary information on the whole site under study, as well as (ii) to (cost-) effectively obtain detail information in areas of interest in order to evaluate in situ remediation options. Overall, the Timbre concept is expected to allow faster and economically more efficient site characterisation, capable of providing reliable site information (which may be a high level of detail, in order to support 2-D / 3-D imaging).

The developed site models provided input for risk assessment and decision support tools (cf. TIMRBE WP6 – Morio, 2014). Phytoremediation is an emerging technology that uses plants and their associated rhizospheric microorganisms to remove, degrade or contain contaminants located in soil, sediments, groundwater, surface water and even the atmosphere (e.g. Chappell 1997; McCutcheon and Schnoor 2003). Successful degradation was also reported for endophytic bacteria (trichloroethene in poplar trees, Weyens et al., 2009). It was found that plants can be used to treat most classes of contaminants, including petroleum hydrocarbons, chlorinated solvents, pesticides, metals, radionuclides, explosives, and excess nutrients. These plants can be herbs, shrubs and trees, and they can concentrate organics and heavy metals at very high levels (Brown 1995; Ma et al. 2000). Until today, however, there are only few examples of successful applications. One reason is that the processes involved are complex, and a full clean up may require many years, so that phytoremediation alone may not be a suitable technology for subsurface contamination. Indirect influences may be of great value, however, as plants affect the water balance of a site, change redox potential and pH, and stimulate microbial activity of the soil. These processes may accelerate degradation in the root zone or reduce leaching of compounds to groundwater (Trapp and Karlson 2001). To date, plants are already in use for the degradation of petroleum products, aromatic hydrocarbons (BTEX), chlorinated solvents, explosives and cyanides. However, phytotoxicity and pollutant mass balances were rarely documented. Often, the success of the projects was not controlled, and only estimates can be made about the applicability and the potential of phytoremediation. This lack of experience about possibilities and limitations seems to be a hindrance for a broader use of these techniques.

Despite the regulatory system is still based on total contaminant concentrations for soil quality assessment, this endpoint has been shown to be irrelevant (Postma et al. 2009) for risks assessment as toxicity is connected to contaminant mobility (Berthelin et al. 2005) to the various environmental compartments (groundwater, atmosphere, living organisms). Contaminants chemical speciation is recognized for long time to be of main importance in risks assessment (for example in the Hazardous Waste Directive 91/689/EEC), but until recently the lack of clear guidance to assess their chemical forms. Considering recalcitrancy, accumulation and bioamplification of priory contaminants, all pathways involved for their transfer should be considered: waterborne, airborne and ingestion routes. Interaction between soil components and contaminants is critical as it is the driving force for retention. In order to assess the contaminant mobility and flow rates from soil matrices (van der Sloot and Kosson 2012; Engelsen et al. 2012) and to anticipate their behaviour under various modifications of physico-chemical parameters (e.g. acidification, oxidation, reduction), suitable leaching tests have been set up considering specifically waterborne transport. The goal of these tests is to get useful information for rapid decisions about risks at negligible costs (in relation to the magnitude of the problem at hand) with respect to treatment costs. The first one is leaching-test, where contaminants are measured in soil-leachates in batch or in column modes, and measures the contaminant mobility to the aqueous medium (or to the aquifer or rivers). Here considering the pH dependence test CEN/TR 14429 aims to study equilibria based release of contaminants from the soil at different pH values, as pH may change due to certain change in conditions such as degree of saturation or ingestion.

For example, the release of metal elements from roads built with solid wastes from municipal incinerators (Francois and Pierson 2009) and recycled concrete wastes used as sub-base in road construction (Engelsen et al. 2012) have been studied. The other one exposed here deals with the buffer-capacity of soil material, which for example, may be affected by acid-leaching of ores under oxidizing conditions or dissolved CO₂ in percolating rainfalls.

Progress in remediation approaches are based upon green technologies and sustainable development, of which the reuse and the recycling of materials are some of the most important principles. Specific soil-flushing with reused fluids (SSFRF) aims at cleaning up contaminant sources in the subsurface, mobilizing pollutants, through the injection (or infiltration) of aqueous fluids (solutions or foams) containing reused diluted (preferably innocuous) extracting agents (Petitgirard et al. 2009; Ahmed Mohamed et al. 2013). To be performed in a reasonable time frame, soil-flushing requires soils with porosity > 20%. A preliminary lab-scale study aims at selecting the best physico-chemical conditions for a selective mobilisation as well as the separation technologies for reuse and recovery, and learning about the extraction mechanism and its kinetic characteristics. A simple and fast treatment of the recovered contaminated fluids using mobile units allows the separation and concentration of pollutants (40-1000 times depending on the separation technology and conditions) to be recycled, while making clean solutions ready to reuse in flushing operations. SSFRS saves for water and chemicals, that are especially suitable for the management of SVOCs and NVOCs (especially in ganglia), and metallic contaminants (Abdul and Ang 1994; Ehsan et al. 2007; Wen et al. 2012), but has been used also for volatile chlorinated compounds (Sabatini et al., 1998; Vane et al. 2001). It is a medium-term remediation technology (weeks to months) limited by the desorption rate of contaminants, targeting diffuse contaminations or ganglia. It can be involved in a technology train (e.g. after pump and treat). Details about the assessment and application of this remediation strategy are provided in D4.4 and selectively below.

Based on the developed site models, a comparative assessment of possible in situ remediation techniques pointed out which measures may, or may not, be successful at the studied Timbre sites. Concerning in situ remediation techniques, phytoremediation, specific soil-flushing and DP-based approaches (injection of microbial substrates or chemical oxidants) were considered in the comparative study.

The aim of this report is to give an overview of the work done with Timbre in WP4, where different strategies and technologies for integrated site characterisation and remediation were investigated. Therefore, the major parts of this report are based on previous deliverables within this WP. An overview of these previous deliverables is given in Table 1. They are in full or shortened versions available on the Timbre project website: <http://www.timbre-project.eu/en/deliverables.html>

Table 1: WP4 related list of deliverables

Deliverable	Title	Public
D4.1 Martac et al. (2013)	Updated site knowledge status (database and site model) as a result of integrated DP and SSP investigation Database and site models implementing updated information from DP/SSP and (potentially) plant investigations (database/model prototype & report)	No*
D4.2 Algreen et al. (2013)	Field test of Tree Coring as an initial screening tool for typical pollutants in the subsurface.	No*
D4.3 Trapp et al. (2014)	Feasibility of phytoremediation for typical pollutants in the subsurface – Report on feasibility testing of phytoremediation for common soil and groundwater pollutants.	Yes
D4.4 Fatin-Rouge et al. (2013)	Feasibility of specific soil washing with recycled solutions (SSWRS) for the removal of selected metals and organic compounds from contaminated soil and mathematical model to assess pollutant transfer by SSWRS	Yes

*A short version or adjusted version is available.

2. Site characterization

Four alternative screening methods to traditional site characterization were applied at two Timbre test sites; Hunedoara and Szprotawa. Data have previously been presented in D4.1 and D4.2, wherefrom major parts of this chapter originate. Furthermore, results obtained at the Szprotawa test site are in the process of publication (Kalisz et al. 2014). Moreover, because toxicity and risks are connected to contaminant mobility, leaching tests and soil buffer capacity were also carried out in the Hunedoara test site.

2.1 Methods

The four alternative screening methods are; tree coring (phytoscreening), soil gas measurements and the two direct push technologies MIP (Membrane Interface Probe) and LIF (Laser Induced Fluorescence). For delineating the hydraulic features of the site, HPT (Hydraulic Profiling Tool) investigations were carried out as well. Figure 1 illustrates the application and the target sampling area of the methods.

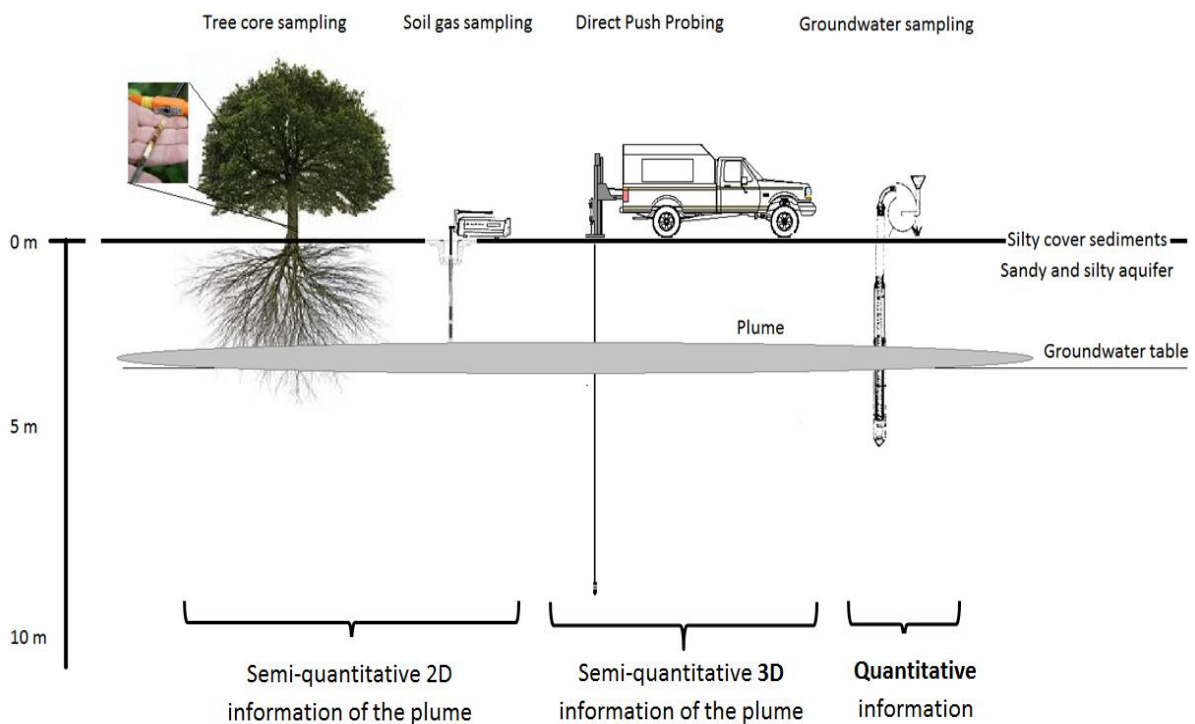


Fig. 1: Representation of sampling methods [modified from pictures found by google].

2.1.1 Tree coring

Chemical compounds can directly be absorbed by the roots, or they enter the roots dissolved in water and then translocated to other parts of the trees. The compounds can then be stored in plant parts above the surface from where tree cores can be sampled and later analyzed. Several guidelines of sampling were published (D 4.2, Holm et al. 2011, Vroblesky 2008). Tree coring is done using a Suunto increment borer and the procedure can be divided into 6 steps; Select a suitable tree, screw the borer into the stem, insert the core retractor, loosening the tree core, remove the tree core sample and transfer to sample storage (Fig. 2).



Fig. 2: The tree coring procedure using a SUUNTO borer [photos by M. Algreen].

The sampling procedure, storage, analysis and treatment of results differ with the compound of interest. Further descriptions can be found in D 4.2.

The extraction of tree cores leaves holes in the stems behind. The trees respond to these wounds with compartmentalization, which includes the process of forming boundaries to isolate the injured tissues, whereby tree coring should not increase the frequency of tree death, even when excessive drilling (Weber and Mattheck 2006).

2.1.2 Soil gas measurement

At the above mentioned Timbre sites, shallow percussion core drillings (2 to 4 m bgl) with simultaneous in-situ soil gas measurements were carried out. The aim of the shallow gas investigation was to correlate and combine it with the data from deeper DP-investigations (soil and groundwater) respectively tree coring. The cores were logged with respect to the geological and geotechnical properties of the subsurface and selected samples were taken and sent to the laboratory for wet chemical analysis. Simultaneous in-situ soil gas measurements were conducted in the percussion drill holes. The drill holes were sealed with a packer unit and the soil gas was subsequently pumped. Relative concentrations of ionisable gases were monitored and documented using a handheld photo-ionisation detector.

In addition, the concentrations of O₂, CO₂, H₂S and methane were measured and documented. Shallow soil gas measurement method can be successfully applied as quick and reliable investigation method able to identify potential source areas in relatively short time gaps.

2.1.3 MIP/LIF/HPT/CPT/EC

The Membrane Interface Probe (MIP) is used for in-situ screening of VOCs (Volatile Organic Compounds) in both the saturated and vadose zone. The MIP cone mobilises a fraction of the VOCs with heat applied from the heating block of the cone. When heated to 120 – 135°C, these compounds are being thermodesorbed and diffuse across the membrane. They are then transported by a carrier gas stream through capillaries in the MIP cable up to the truck where they are continuously detected with a gas chromatograph equipped with a PID (Photo Ionisation Detector), an FID (Flame Ionisation Detector) and a DELCD (Dry Electrolytic Conductivity Detector). This detector combination allows for selective specification of the contaminant type. The MIP unit was equipped with a heated trunkline to increase sensitivity and to reduce detector tailing effects caused by condensation or retardation.

Laser Induced Fluorescence (LIF) is a tool that detects Polyaromatic Hydrocarbon (PAH) bearing oil compounds. PAH fluoresce if they are excited by light of a specific wavelength. This excitation leads to light emission in a certain wavelength range which is called Fluorescence. As PAH occur in all types of oil (sometimes in very small amounts), LIF is able to detect every contamination caused by oil derived hydrocarbons, i.e. jet fuel, diesel, petrol, mineral oil, tar, creosote, etc. Every shot of the laser causes light emission in a certain wavelength range. The total fluorescence intensity is the sum of four specific emission wavelengths. Every oil type has its own characteristic wavelength pattern or „waveform“. The difference between lighter hydrocarbon mixtures like petrol, kerosene or diesel, where the lower wavelengths predominate, and the heavier hydrocarbons e.g. tar or creosote, where the higher wavelengths predominate, can be clearly seen.

Hydraulic Profiling Tool (HPT) is a system designed to evaluate the hydraulic properties of the site subsurface. The probe is advanced through the subsurface (at cm/s) while water is injected at a constant rate Q (ca. 250-2000 ml/min) through a screen on the side of the probe. An in-line pressure sensor measures the pressure response p of the soil/groundwater system against water injection. The water flows into the layers in a more or less easy way, depending on hydraulic properties of the soil. A relatively low pressure response indicated a relatively large grain size, and the ability to easily transmit water. A relatively high pressure response, however, indicates a relatively small grain size and the inability to transmit water. Pressure and flow rate are both logged versus depth. In order to discard the potential effects of the flow rate variability, the interpretation of the recorded profile is preliminary judged in terms of Q/p as relative hydraulic conductivity.

Since the HPT pressure response is analogous to relative changes in the ability to transmit water (and therefore the relative change in dominant grain size), the HPT system can be used to identify potential contaminant migration pathways. Similarly, it can help to identify zones for remedial material injection or provide qualitative guidance on how difficult injection may be in different zones of the formation.

Cone Penetration Testing (CPT) is able to determine the physical soil properties and identify the site specific lithology.

The electrical conductivity probe (EC) allows the user to collect soil electrical conductivity data used to infer the lithology.

2.1.4 Leaching tests for soil characterization

The pH-dependent leaching potential behaviour for contaminants was assessed according to the CEN/TS14429 method with a liquid to solid ratio (L/S) of 10. The neutralisation potential (NP) and the acidity potential (AP) for the soils were carried out in batch mode according to the CEN/TC292 EN15875 method, which assesses soil-buffer capacities for sulphide ores. These measurements were carried out on two top soils samples called EC1 and E3. Each field sample was collected from the surface layer (0-0.2 m) using a shovel and was immediately sieved to 2 mm. EC1 was a mixture obtained from seven soil samples collected all over the field-test, selected for their aspect. E3 was collected from a few meter square area and was selected as it appeared to be a hot spot from its colour and composition. Leaching tests for metals and organic carbon (TOC and TPH) were carried out both in column (dynamic mode) and in batch (static mode) as a function of pH. For column leaching tests, 2.0 g of soil samples were introduced in a burette, then 20.0 ml of distilled water with pH in the range 2-12 was percolated through the samples. In the batch mode, 10.0 g of soil were mechanically mixed with 100.0 ml of distilled water with pH in the range 2-12 for 48 h using a vibrating table. pH were readjusted at the flowing times: 2, 4, 8, 16, 32, 48h with HNO₃ (70%) and NaOH (5 M).

Total concentrations for metals and organic contaminants (TPH, BTEX, PAH) were determined in each soil sample. All soil leachates were immediately filtrated through Whatman n°4 filter paper. ICP-OES was used to measure concentrations of elements Al, As, Ba, Ca, Cr, Cu, Fe, Mn, Pb and Zn, both in soil samples after mineralization with aqua Regia and in leachates after acidification (pH < 2, HNO₃ Suprapur). Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) in soil leachates was measured using a Shimadzu TOC analyser. Inorganic carbon concentrations in samples were determined according to the official method EN 13137:2001. EC1 composite soil sample was characterized by X-ray diffraction with a Brucker AXS diffractometer using the Cu-K_α emission. Patterns were recorded over a 2-θ range of 10-90°. The most abundant mineral phases were identified as quartz, illite, α- and γ-Fe₂O₃ and MnO.H₂O or Mn(OH)₂.

2.2 Test sites and application

All screening methods were applied at the two Timbre sites Hunedoara (Romania) and Szprotawa (Poland). The test site in Hunedoara is located in the South-West area of Hunedoara (Fig. 3A). The site is a former steel works, and industrial activities were carried out on the site between 1884 and 1999. The site is polluted with heavy metals, BTEX and PAHs. The second test site located in Szprotawa is the former air base founded in the early 1930s (Fig. 3B). After World War II, the air base was taken over by the Soviet Army that used it until 1992. After the withdrawal of the Soviets, the air base was closed down and the area was converted into a civilian facility. The site is polluted with BTEXN. Additional pictures from the test sites can be seen in Fig. 4.



Fig. 3: A) Aerial view of the Hunedoara test site and the main sampling area. B) Overview of the Szprotawa test site. (Modified from Google Maps).

Hunedoara, Romania



Szprotawa, Poland



Fig. 4: Pictures from the two Timbre test sites Hunedoara and Szprotawa (Photos by M. Algreen).

Table 2 gives an overview of the application of the different screening methods at the two test site.

Table 2: Overview of sampling numbers and year at the two Timbre test sites.

	Hunedoara, Romania			Szprotawa, Poland		
	Sampling number	Year	Note	Sampling number	Year	Note
Tree coring	21	2011	Poplars, willows	27, 21, 9 17, 18	2012 2013	Pine, birch, willow Willow, asp
Soil gas						
MIP				14	2012 2013	
LIF				26	2013	
HPT	16	2012				
Leaching tests	10	2011				

2.3 Results

2.3.1 Hunedoara

2.3.1.1 Tree coring

At Hunedoara, the tree coring method was tested as a bioindicator for both heavy metals and BTEXN compounds. The analytical data of the two compounds groups have to be treated differently (see D 4.2) – therefore, the results will be presented separately below.

Heavy metals. The sampling was done without knowing much about the heavy metal level at the site beforehand. The samples were therefore collected all over the site and allocated to subareas (I-VIII, see Fig. 5). The average concentrations of each subarea are shown in Table 3. Most of the average concentrations of the test site are above the average concentrations of the reference samples.

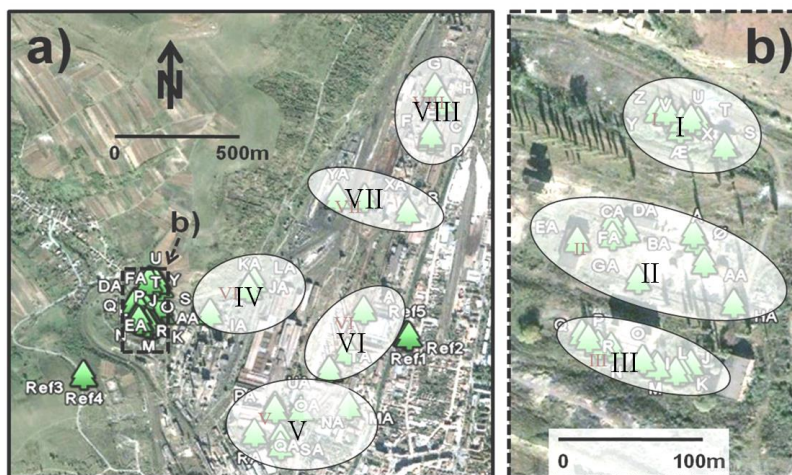


Fig. 5: Map of the Hunedoara test site showing the subareas used to evaluate the pollution of heavy metals. b) is a zoom into a) (Modified from Google Earth).

Table 3: Average concentrations measured in the trees from each subarea

indicates a higher average concentration in the samples from the test site compared to those of the references site. Italic indicates a lower average concentration measured at the test site compared to the reference sites.

	Reference areas	Area I	Area II	Area III	Area IV	Area V	Area VI	Area VII	Area VIII
Cd	0.27	0.16	0.53	0.27	0.37	0.24	0.29	0.18	0.35
Cr	0.24	0.34	0.28	0.42	0.30	0.28	0.28	0.40	0.66
Cu	1.58	1.34	3.62	1.31	2.67	1.76	3.12	1.64	1.15
Mn	4.69	4.32	25.65	5.36	9.29	3.92	7.39	12.10	7.25
Ni	0.20	0.18	0.16	0.27	0.39	0.29	0.20	0.21	0.30
Zn	18.40	15.3	27.3	23.5	28.1	18.6	27.8	26.8	19.1

To test the feasibility of the screening method, a two-tailed t-test with an error probability of 0.05 ($\alpha = 5\%$) was applied to determine significant differences between the average concentrations of each subarea and the reference samples. The results are shown in Table 4 and Fig. 6:

- No elevated levels of heavy metals are found in the areas of V and VII.
- The Cd levels of area II and VIII are significantly higher compared to the reference samples.
- The Cd levels of area I and VII are also significantly different to the reference, but the average concentration in the tree cores are highest in the reference samples
- The Cr levels of area I, III, VI and VIII are significantly higher compared to the reference samples.
- The Cu levels of area II and IV are significantly higher compared to the reference samples.
- The Mn levels of area II, IV, VI and VIII are significantly higher compared to the reference samples.
- The Ni level of area IV is significantly higher compared to the reference samples.
- The Zn level of area II is significantly higher compared to the reference samples.

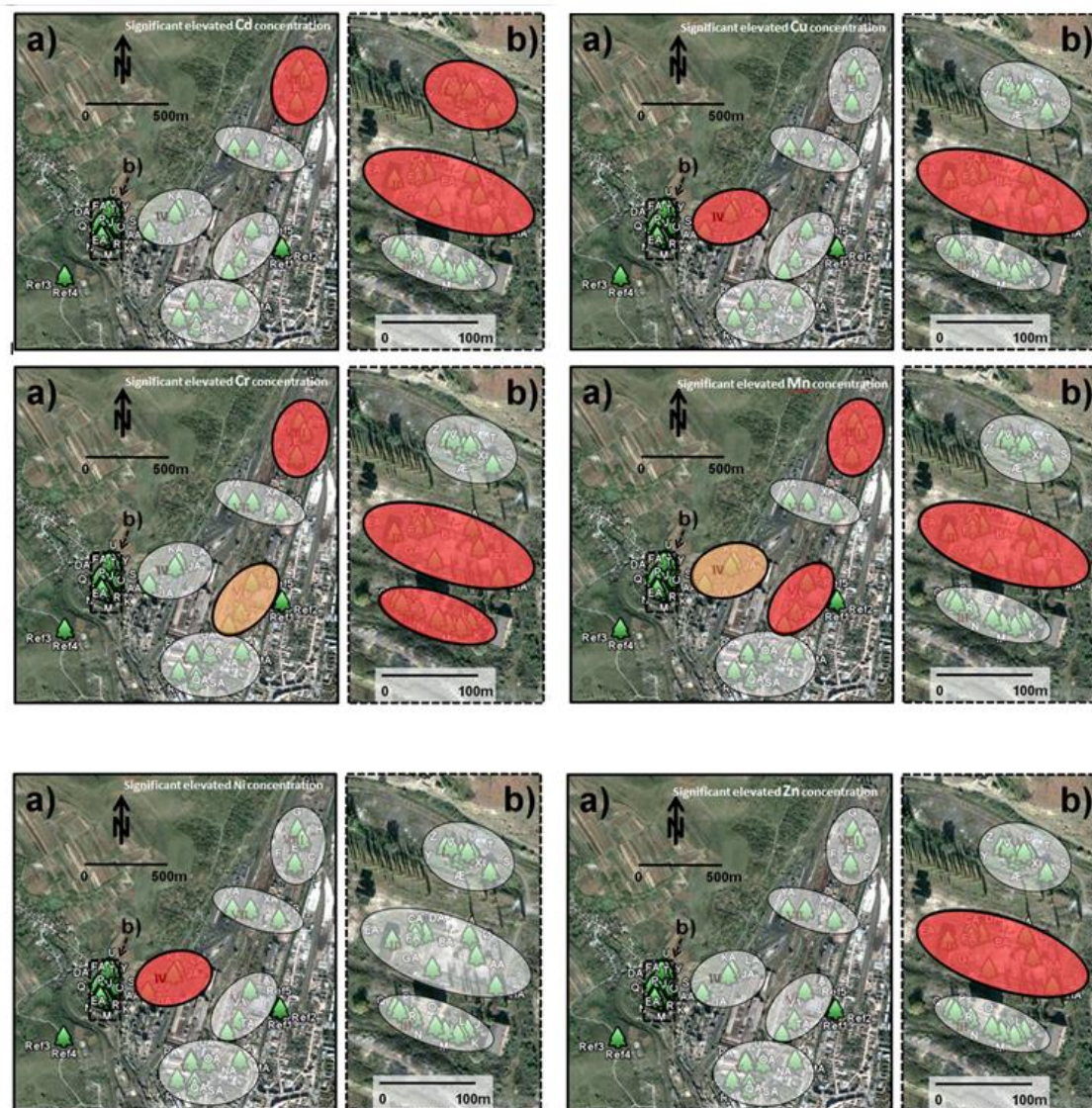


Fig. 6: Overview of subareas with increased concentrations of Cd, Cu, Cr, Mn, Ni and Zn measured in wood. (Modified from Google Earth)

Table 4: Statistic test of significant differences between the reference area and the test subareas. Bold indicates significant difference ($\alpha=5\%$, $\ast\alpha=10\%$) between the concentration measured in the reference wood and the wood from the test site subarea. Italic indicates significant difference between the samples, but with highest concentrations in the reference samples.

	Area I n=26		Area II n=30		Area III n=30		Area IV n=18		Area V n=23		Area VI n=18		Area VII n=16		Area VIII n=22	
	T-value – Significant or not.															
Cd	0.000	Yes	0.001	Yes	0.840	No	0.192	No	0.565	No	0.829	No	0.006	Yes	0.078	Yes
Cr	0.029	Yes	0.120	No	0.000	Yes	0.257	No	0.210	No	0.099	Yes*	0.155	No	0.018	Yes
Cu	0.455	No	0.003	Yes	0.416	No	0.025	Yes	0.621	No	0.206	No	0.899	No	0.206	No
Mn	0.700	No	0.000	Yes	0.284	No	0.051	Yes*	0.126	No	0.047	Yes*	0.125	No	0.047	Yes
Ni	0.754	No	0.504	No	0.302	No	0.026	Yes	0.154	No	0.888	No	0.889	No	0.220	No
Zn	0.370	No	0.041	Yes	0.316	No	0.150	No	0.966	No	0.159	No	0.264	No	0.814	No

BTEXN. Tree coring as a phytoscreening method was tested in the initial phase in order to answer to the starting question: can the compound be detected or not in the wood? BTEXN compounds have been detected in four out of 21 samples, all in the high risk area (Fig. 7). For benzene, even different levels were observed (Fig 7B). This indicates that the trees are able to take up BTEXN compounds from the subsurface and transport them to the stem where they can be detected.

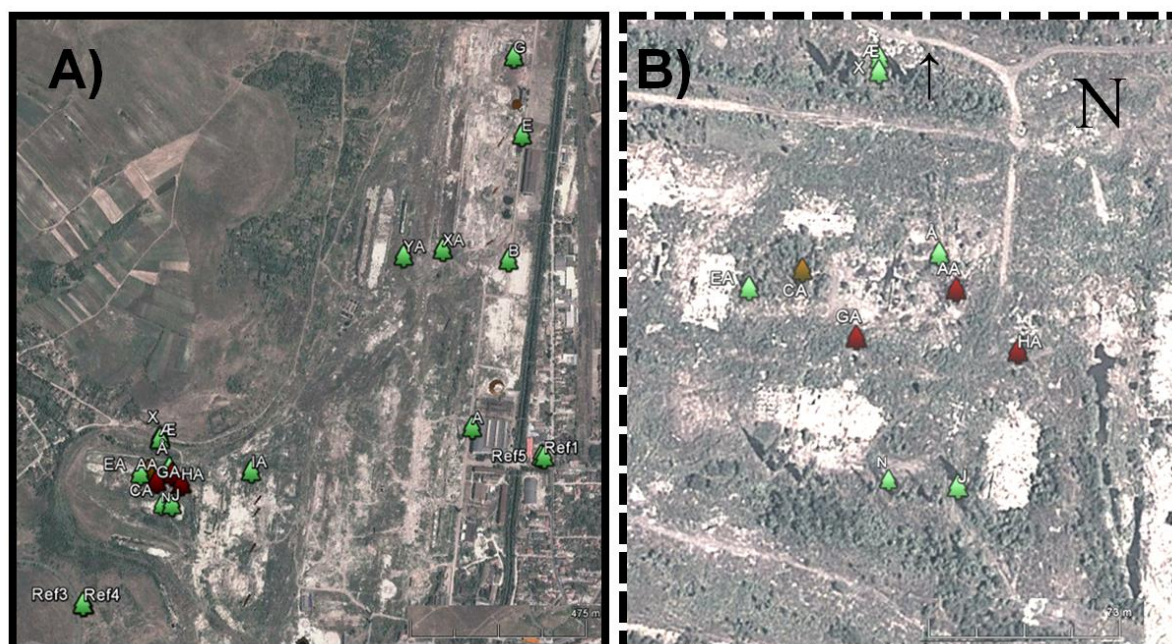


Fig. 7: Map of tree core samples analysed for BTEXN. Green icons indicate that no compounds were detected, yellow icons indicate that toluene was detected at low levels and red icons indicate that one or more compounds were detected. b) is a zoom of a). (Modified from Google Earth)

2.3.1.2 Soil gas measurements

The 51 percussion holes drilled down to 2 m bgl served for a good geotechnical description of subsurface and for reliable soil gas measurements as well as for the investigation of heavy metals presence and distribution in top soil (0-20 cm) and in depth (1-2 m). High concentrations of ionizable gas (naphtalene) were measured in vicinity of remnants of tanks. Generally low soil gas values were detected throughout rest of area (clay layer!). Higher values of heavy metals were measured throughout the investigated area (Zn, As, Cu, Ni, Pb, Cd) but vertically limited mostly to top soil (0-20 cm). In depth (1-2 m) generally low values are present. All DP related activities and analyses are fully documented in Appendix 2, D4.1.

2.3.1.3 DP-HPT

During the September 2012 campaign, a second sequence of soil sampling events (open window sampling and Direct Push Liner sampling) followed by Direct Push based hydraulic profiling tool investigation and installation of monitoring wells was carried out. The geological model was based on 30 boreholes lithological logs (and in some cases the HPT profile and the Electric Conductivity) coming from the site investigations performed by Fugro Consult GmbH in two campaigns (23 boreholes) and also from previous studies. Accordingly with the point information (boreholes logs) for Hunedoara site, the aquifer geometry was derived (bottom, top and thickness), hydraulic properties distribution maps (based on lithological information, HPT log (Fig. 8) and grain size distribution values on 18 samples, hydrogeological map (groundwater level) - based on groundwater and surface water measurements.

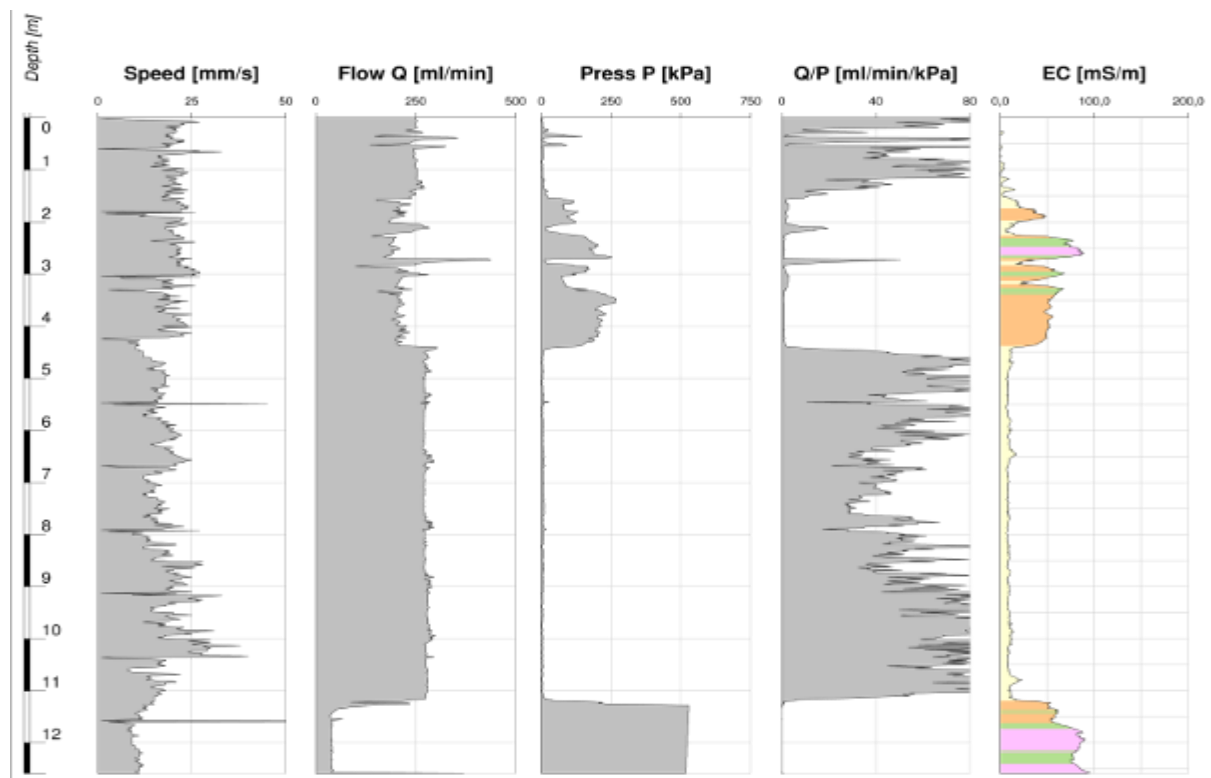


Fig. 8: Typical hydrogeological features (grain size distribution, aquifer geometry, hydraulics) at Hunedoara site

2.3.1.4 Contamination - soil and groundwater

The major contamination issue for Hunedoara area are the heavy metals. Also other contaminants can be found in the soil and in the groundwater in significant concentrations (naphthalene, benzene).

Regarding the soil contamination (Table 1, D4.1) for the superficial part (from 0-1 m) it was observed that two heavily contaminated areas were identified:

- (1) northern part of the site - the former chemical plant; and
- (2) former phenol water treatment plant. In these areas, the values for most of the contaminants overpass the intervention limit.

In the rest of the area, the pollution is caused mainly by heavy metals compounds.

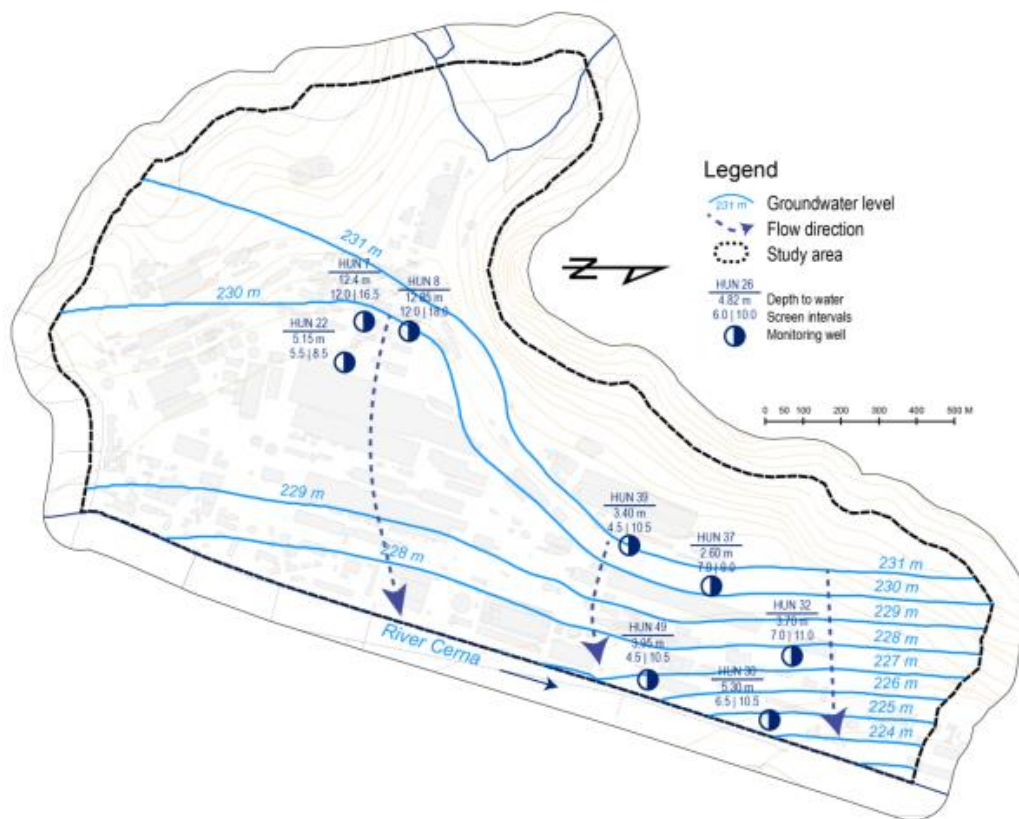


Fig. 9: Groundwater flow direction within area of interest

Due to the clay layer that seals the aquifer, the groundwater is less polluted. The main flow directions are defined based on the Timbre newly installed groundwater monitoring wells (Fig. 9).

2.3.1.5 Leaching tests

In the case of the former iron-smelter Hunedoara site, many organic and inorganic contaminants were present in soil as well as high amounts of metal sulphides in top soil coming from mining material. Leaching tests were carried out in a large pH-range to assess mobilisation potential under various conditions (and hence risks) for the identified contaminants (mainly heavy metals) and the soil-buffer capacity with respect to acid leaching. These tests were carried out on composite-soil samples collected all over the site, on a sulphide rich top soil (E3) found in the former chemical plant area, and on heavily contaminated soils in the former wastewater treatment plant (N3).

The composite sample provides general site characteristics about the behaviour of contaminants and the soil. **The costs associated to these analyses are negligible with respect to remediation costs and thus potentially save for huge remediation costs.** Hence, leaching tests were performed for risks assessment associated to untreated soils and soil-flushing operations.

Fortunately, thanks to the large amount of materials like illite and Fe(III) oxides with high sorption capacity and inertness (Bertelin et al. 2005) in the upper part of the underground, heavy metals were not detected in groundwater despite elevated concentrations in top soils. As shown in Fig. 10, the leaching potential of the main inorganic contaminants is low and correlated to the leaching of iron. Main leached substances are DOC (70-80 mg l⁻¹), Fe (~ 5 mg l⁻¹) and Mn (~0.5 mg l⁻¹), in qualitative agreement with groundwater measurements. The increase of DOC with pH is a general tendency observed everywhere in the site, but easily explained by the presence of carboxylic and phenolic functions like for natural organic matter. Metal-leaching increased by 1-3 orders of magnitude as pH decreased to pH 2-3. This could be the result of iron mobilization or proton competition for illite, as its pH for charge neutralization is 2.5 (Hussain et al. 1996). The enhanced mobilization of Cu(II), Cr(III) and Pb(II) in alkaline solutions is usually linked to the increase in DOC, as it bears binding moieties. Fortunately, in contrast to E3, the soil-buffer capacity for EC1 was enough to prevent acid drainage from sulphide oxidation. Soil N3 were characterized by the presence of a free non aqueous phase. TPH concentrations in aqueous solutions contacted with soil were about 7 mg l⁻¹ at neutral pH, but increased up to 20 mg l⁻¹ at pH 11.

In the case of surfactant aided soil-flushing for example, leaching tests have showed that despite 95% TPH can be removed from the soil, their leaching potential has been increased by 2 orders of magnitude! Hence, a careful removal of extracting agents is required at the end of the treatment. Moreover, metal-leaching appeared to be critically dependent on the surfactant used. Non-ionic surfactants are better for the selective mobilization of hydrocarbons, as the other stabilize in solution a substantial amount of metals too.

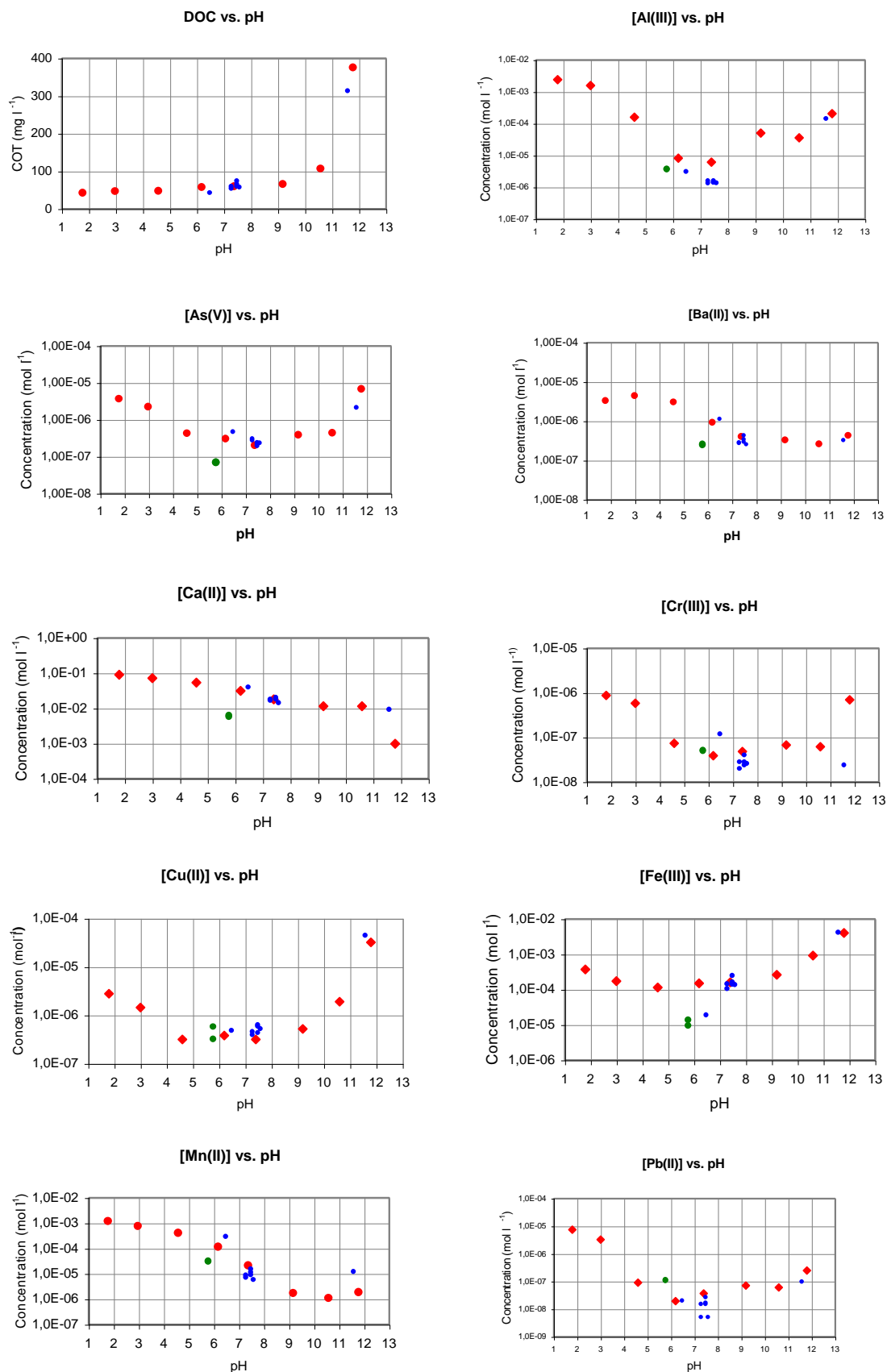


Fig. 10: Metal and DOC concentrations in leachates for static (red marks) and dynamic (green (E3) and blue (EC1) marks) leaching tests. Note: Cr(VI) was not detected

2.3.2 Szprotawa

2.3.2.1 Tree coring

Tree core sampling was performed both in 2012 and 2013. In the first sampling campaign, mainly samples from pines and birches were collected. The results showed that only toluene could be detected in these tree cores. Toluene was detected in one birch (from the high risk area) out of 21 (14 in the high risk area) with a concentration below the quantification limit, and in 16 pines (12 in the high risk area) out of 27 (15 in the high risk area), see Fig. 11.

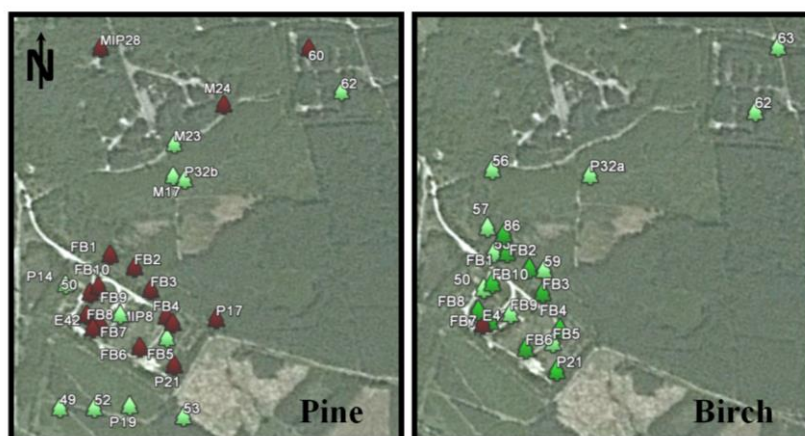


Fig. 11: Results overview of pines and birches test trees (2012). Green symbol indicates no compounds were detected and red symbol indicates that toluene was detected (Modified from Google Earth).

In the second sampling campaign, aspens and willows were collected and toluene was detected in all samples, ethylbenzene, m, p, o-xylene were detected in most or the samples (26 and 24 out of 35 samples, respectively) and benzene and naphthalene in some or the samples (eight out of 35 samples). From Fig. 12, it can be seen that the samples containing BTEXN all are from the southern corner of the main high risk area (former gas station).



Fig. 12. The symbols indicate that following compounds detected in the tree cores (2013): red = BTEXN, light blue = BTEX, blue = TEXN, yellow = TEX, purple = TX, light green = TE, dark green = TN, white = toluene. (Modified from Google Earth).

The different tree species were compared. 14 pine/birch sets (trees of each species located within 2 m from each other, one set from outside of the high risk zone) and nine willows were sampled in 2012, and ten willow/asp sets were collected in 2013. Results are shown in Fig. 13. When comparing the pine/birch sets, it became clear that pines are better indicators for toluene soil contaminations than birches. This was concluded by the fact that toluene was detected in only one of the birch samples (below the quantification limit) compared to toluene concentrations found in 11 pine samples (four below the quantification limit). The results from the willow samples indicate that other compounds than toluene can be detected in this tree species. Therefore, willows may be more feasible for phytoscreening of BTEXN compounds than pines and birches.

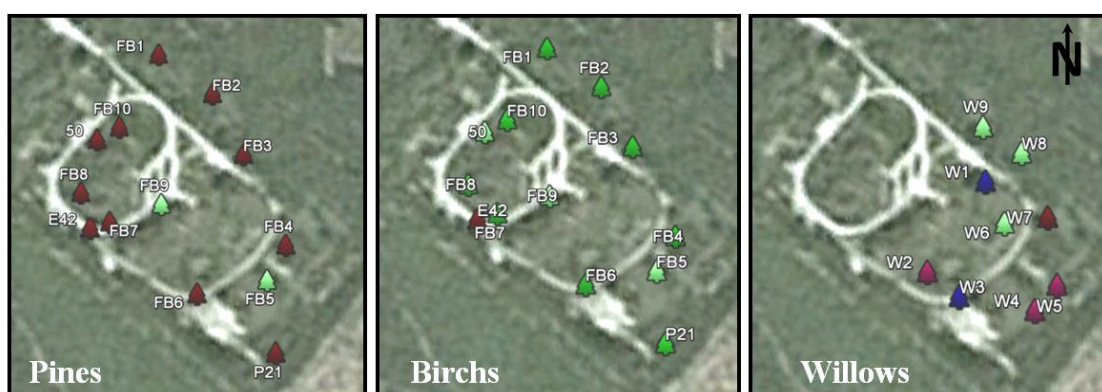


Fig. 13: Results overview of pine, birch and willow test trees in the high risk area (2012). The symbols indicate that the following compounds are detected in the tree cores: green = no compounds, red = toluene, blue = other BTEXN compounds than toluene, pink = toluene and other BTEXN compound. (Modified from Google Earth).

The results from willows and asps (2013) were analysed through a rank correlation. A significant correlation between the tree species cannot be proved (correlation value = 0.3576). Interpolation plots of the data from the willow/asp sets are presented in Fig. 14. Both tree species indicate an increased BTEXN level in the main high risk area.

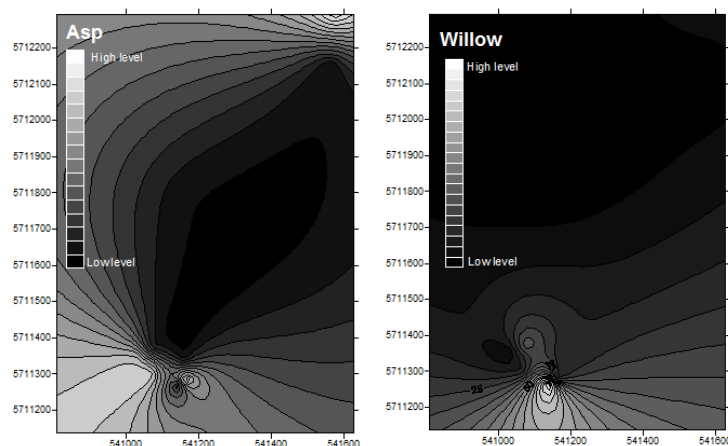


Fig. 14: Interpolation plots of data obtained from willows and asps at the same sampling points.

2.3.2.2 Soil gas measurements

Soil gas measurements gave a solid overview for contaminant characterization of the study area. High concentrations of ionizable gas were detected in central fueling area and around fuel tanks in paint ball area (Fig. 15, Fig. 16). Possible subsurface pollution along the supply pipes was identified. The method proved to be a fast and cost effective choice for identifying hot spots. High concentrations of hydrocarbons were measured in soil samples from central fuelling area with typical kerosene pattern. Traces of chlorinated organic compounds were also detected.

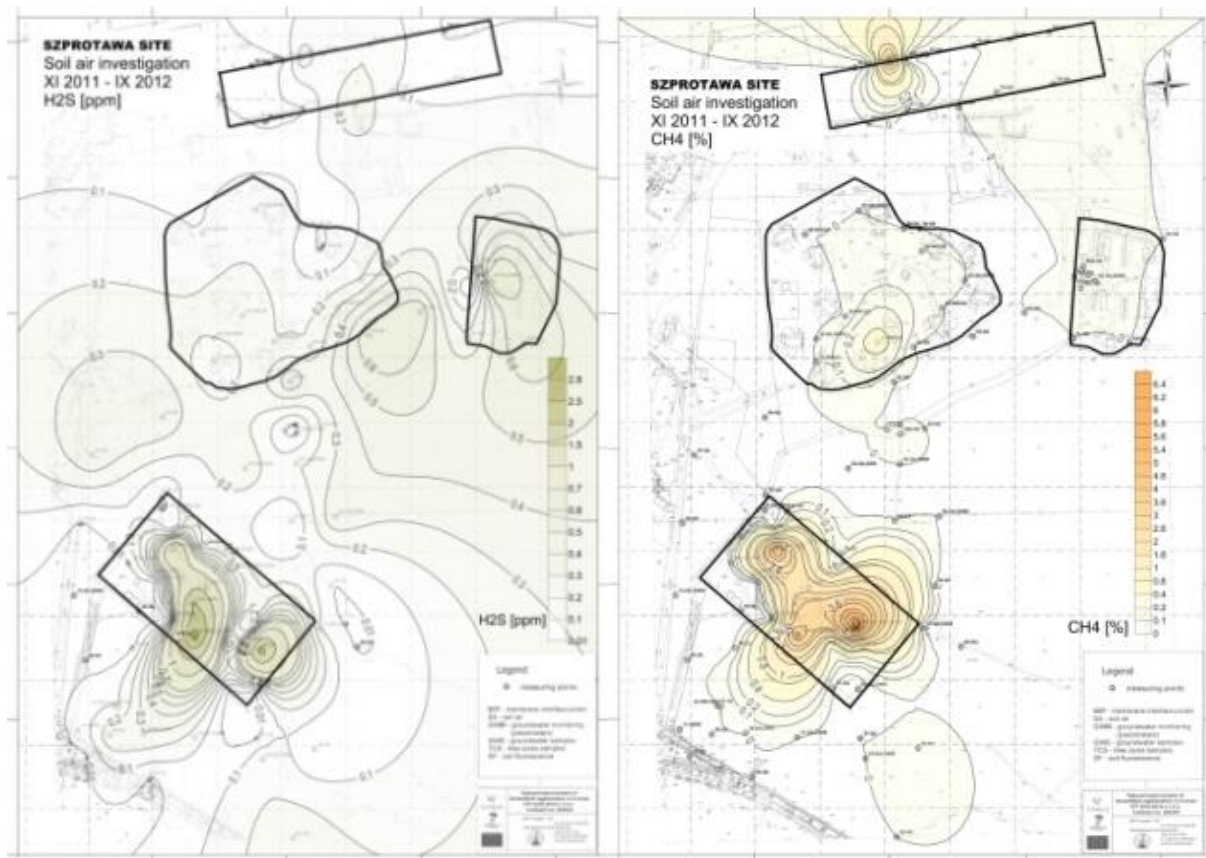


Fig. 15: Contaminant distribution based on soil gas investigation

2.3.2.3 MIP/LIF

Direct push investigations including Membrane Interface Probe (MIP), Laser Induced Fluorescence (LIF), groundwater and soil sampling, installation of groundwater monitoring wells for long time monitoring and Slug testing for hydraulic properties of the subsurface were carried out during several field campaigns. Using a Geoprobe DT6620 drilling rig with optional anchored bridge for the hydraulic hammer, the area of former gas station was characterized by MIP and LIF technologies. The neighboring area outside of the gas station zone was investigated by MIP. 14 MIP profiles and 26 LIF profiles were carried out.

Fig. 16 shows a very good vertical differentiation of the area where very high benzene concentrations (LNAPL) are present. All Direct Push related activities are fully documented in Appendix 1, D4.1. A site map with the location of the investigation points is presented on the Timbre Internet site under the Szprotawa GIS project.

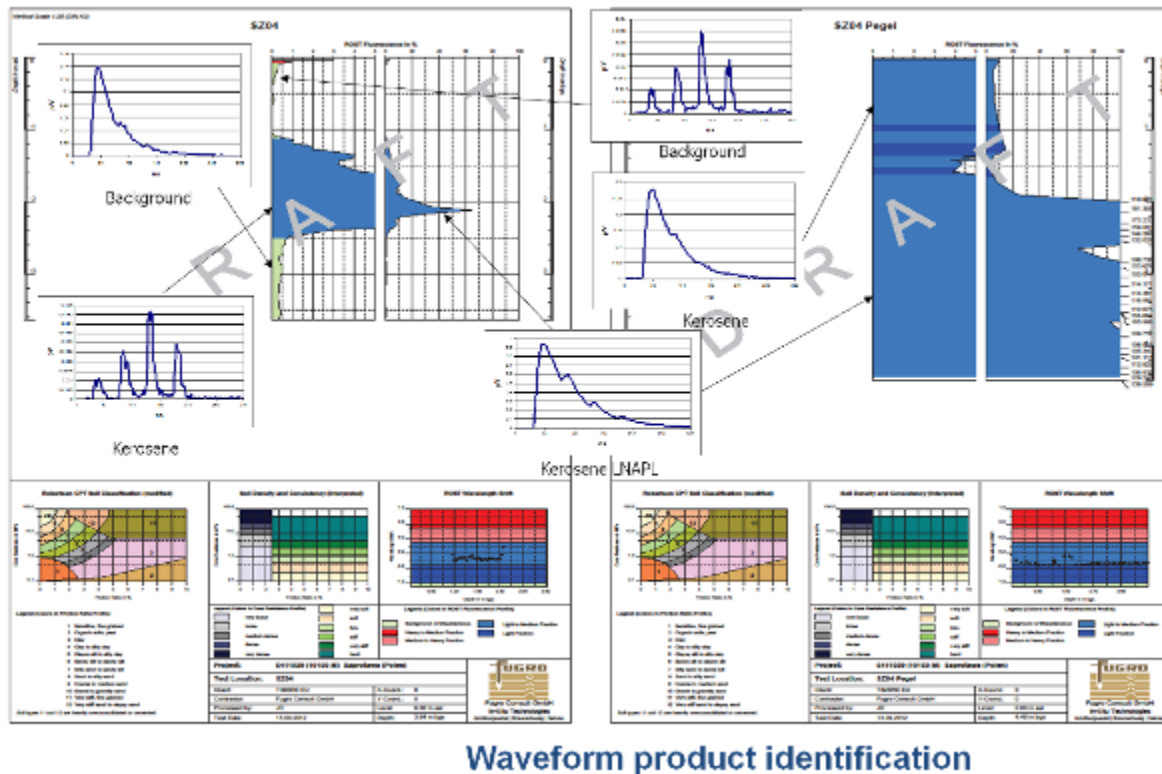


Fig. 16: Results of Direct Push (LIF) investigations

The source areas were very well delineated by LIF signals (Fig. 16), areas with residual kerosene as NAPL were identified (Fig. 17). A 3D evaluation of the spatial extension of the kerosene body still present at the site (Szprotawa) is carried out, including an estimated of kerosene mass and volume.

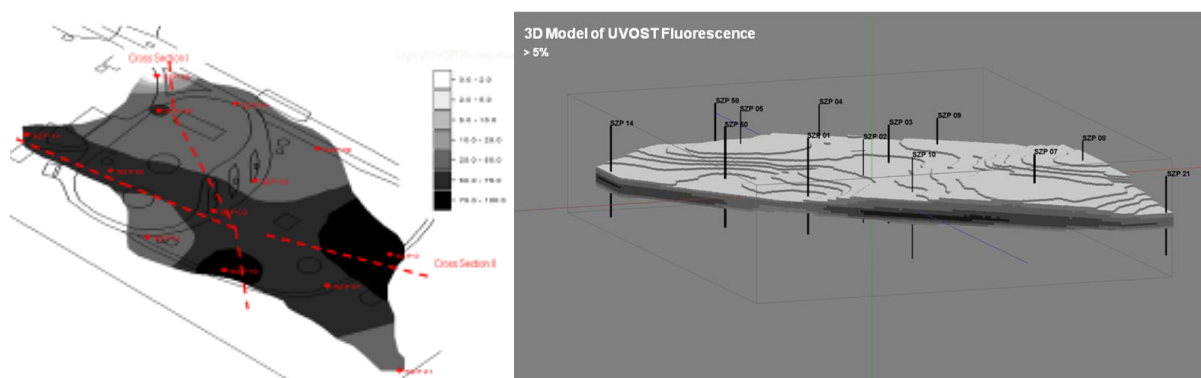


Fig. 17: Spatial distribution of NAPL within the former tank area

Based on the Timbre newly installed monitoring wells, a spatial distribution of the contamination as diluted phase in groundwater was delineated (Fig. 18).

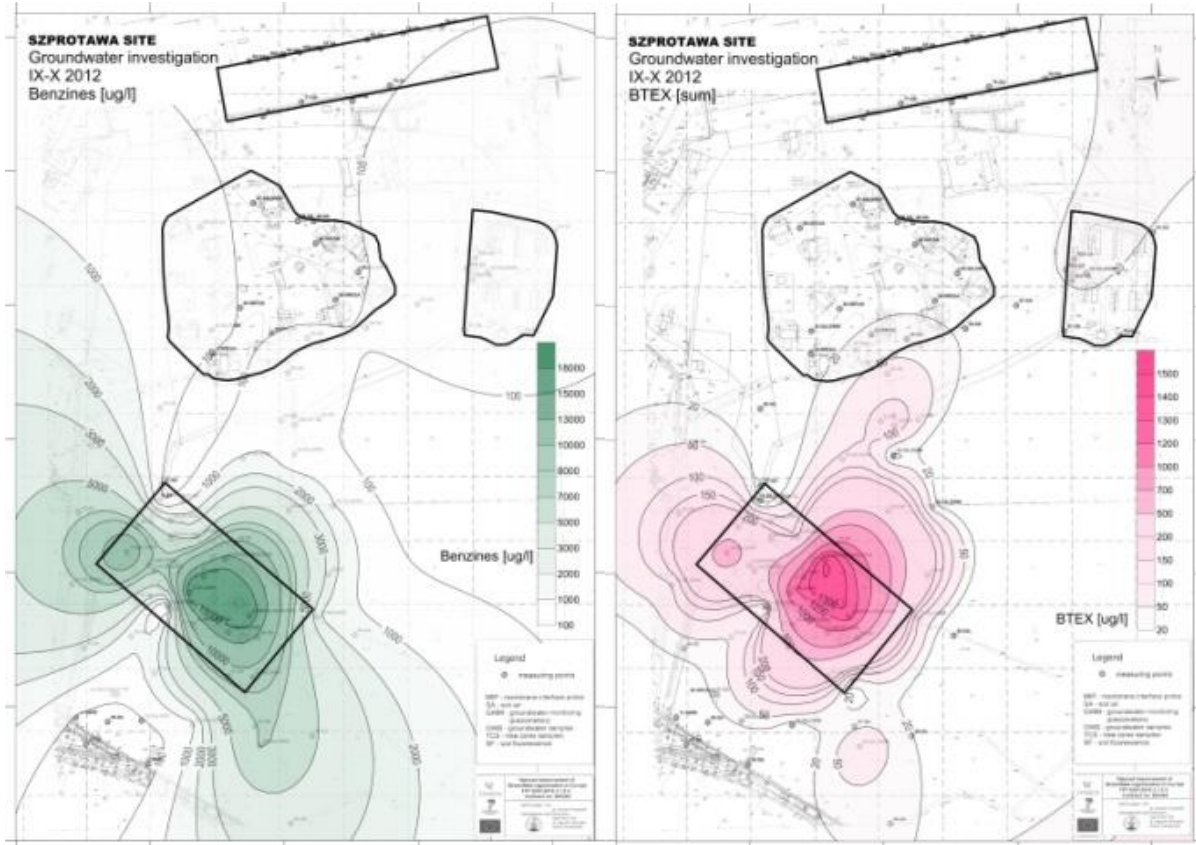


Fig. 18: Contaminant distribution based on groundwater analyses

3. Site remediation

The aim of the Timbre project was to develop and provide customized problem- and target-oriented packages of approaches, tools and technologies to overcome existing barriers to mega-sites regeneration.

Soil-washing and soil-flushing are two leaching technologies available to remove contaminants from soils. They differ by the fact that the former needs excavation, while the latter is carried out in-situ. Despite soil-washing is more effective to remove contaminants thanks to mechanical effects such as convection and grinding, the absence of excavation, handling and transport of contaminated materials makes soil-flushing preferred and advised. So, Timbre team focused onto soil-flushing, as it is more challenging because it is more difficult to control, especially regarding to efficiency. However, leaching of contaminants from soils is expensive, accounting for chemical and wastewater treatment costs. For VOC contaminants it is advised to remove NAPL by pumping as long as it is effective. In this situation, soil-flushing may be used after the pump and treat to help for recovery of residual contaminants in low porosity / low accessibility zones. However, because the use of surfactants, wastewater treatment is much more difficult and expensive, as contaminants are solubilized in water. Within Timbre the aim of this work was to assess the SSFRF approach in terms of benefits, costs and risks. More accurately, the goals were to reduce costs by:

- making leaching fluids more effective,
- re-using chemicals and leaching fluids and making a spate of uses,
- recycling leaching fluids for other washing operations and for energy recovery.

D4.4 focuses onto the treatment of contamination with SVOCs like PAHs, because metal contaminants were either absent (Solec Kujawski test-site) and or did not match soil-flushing because of their huge amount and inertness (Hunedoara test-site). However, the extraction of heavy metals from model contaminated soils has been successfully carried out and assessed (Mohamed et al. 2013; Efligenir et al. 2013). The two selected sites offered extreme conditions in terms of contaminant concentrations and soil properties, which allowed the assessment of SSFRF in a wide range of situations.

Timbre research on phytoremediation (see D4.3) aimed at filling major knowledge gaps that have hampered a wider application of this technology so far. The feasibility of phytoremediation was investigated systematically for common soil and groundwater contaminants. Toxicity data (mainly for willows) were derived, and metabolism experiments were carried out *in vivo* and *in vitro* in order to determine plant degradation rates. Important research questions are whether degradation is due to microorganisms (root zone bacteria or endophytic microbes) or plants, and which parameters and processes are rate-limiting. Chemical plant uptake was investigated based on measured data and modelling, delivering input for exposure estimation and risk assessment concerning potential applications of this technology. Time scales required for phytoremediation were estimated using mass balance models, and potential optimisations (combination with other methods) were evaluated.

Aims were to elucidate under which conditions phytoremediation is an appropriate and (cost-) effective option, when it should be applied and when it might fail or be too slow. Based on our set of experiments and model calculations, assessments were provided in order to judge success, time scale and risks of phytoremediation.

3.1 Methods

3.1.1 Soil washing

Detailed description of Timbre research activities related to soil-flushing are provided in D4.4. Selection of in-situ treatment mainly depends on contaminant volatility. Whereas in-situ physical technologies (e.g. soil vapour extraction (SVE), thermal desorption) are able to remove volatile contaminants, they are ineffective to deal with SVOCs and NVOCs. The latter require chemicals to be degraded (e.g. redox reagents) or mobilised, and fluids (or mixing with soil) to ensure contact and reaction. However, the use of solutions must be carried out cautiously to avoid cross-media contamination by migration in groundwater and leakage from the top soil surface if recovered leachates are mismanaged. Extraction fluids must be recovered, usually using physical or hydraulic barriers in unsaturated and saturated zones respectively as shown in Fig. 19. Site characterisation is specially required. Geological data are needed to assess the homogeneity and the anisotropy of the subsurface. Hydrological data allow determining groundwater characteristics (water table and variations, groundwater flow). Groundwater flow is of main importance with respect to dilution factors and the interest in using specific concentration technologies with benefit. It is obtained through the measurements of hydraulic conductivity and porosity of the soil, and the hydraulic gradient of groundwater. When groundwater extraction is needed, pumping tests must be performed to assess safe aquifer yields and to set boundary conditions.

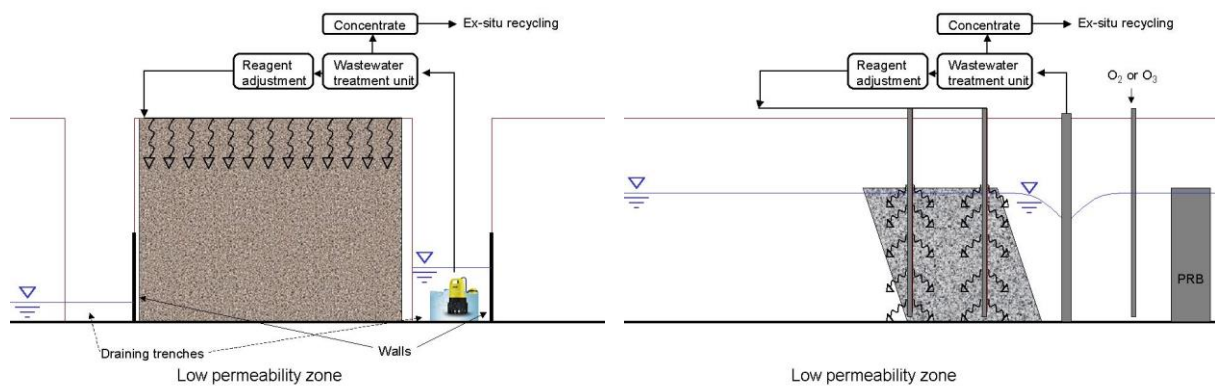


Fig. 19: Schematic pictures for usual soil-flushing treatment set-up

Soil-flushing is a high potential in-situ technology, with minimal site disturbance, able to adapt easily to target contaminants by using additives that help for their removal. Site characterisation of all leachable contaminants must be carried out before remedial action, in order to set-up a suitable treatment of recovered fluids. In addition, soil conductivity ($> 10^{-5} \text{ cm s}^{-1}$) is critical to allow percolation in a reasonable time-scale, whereas groundwater level and the presence of free phases should be identified first. In case of free phase, a preliminary pump and treat is required to remove it. The selection of optimal physico-chemical conditions (e.g. pH, reagents, concentrations) are required to ensure efficiency. However effectiveness is not the single selection parameter. Several other should be taken into account as detailed below. They are of importance with respect to the safety of workers and environmental medium, to ease the management at the end of remedial step, and to carry and monitor the remedial action at the lowest cost. A flow chart is provided below (Fig. 20) to help for the decision process concerning the use of SSFRS in soil remediation.

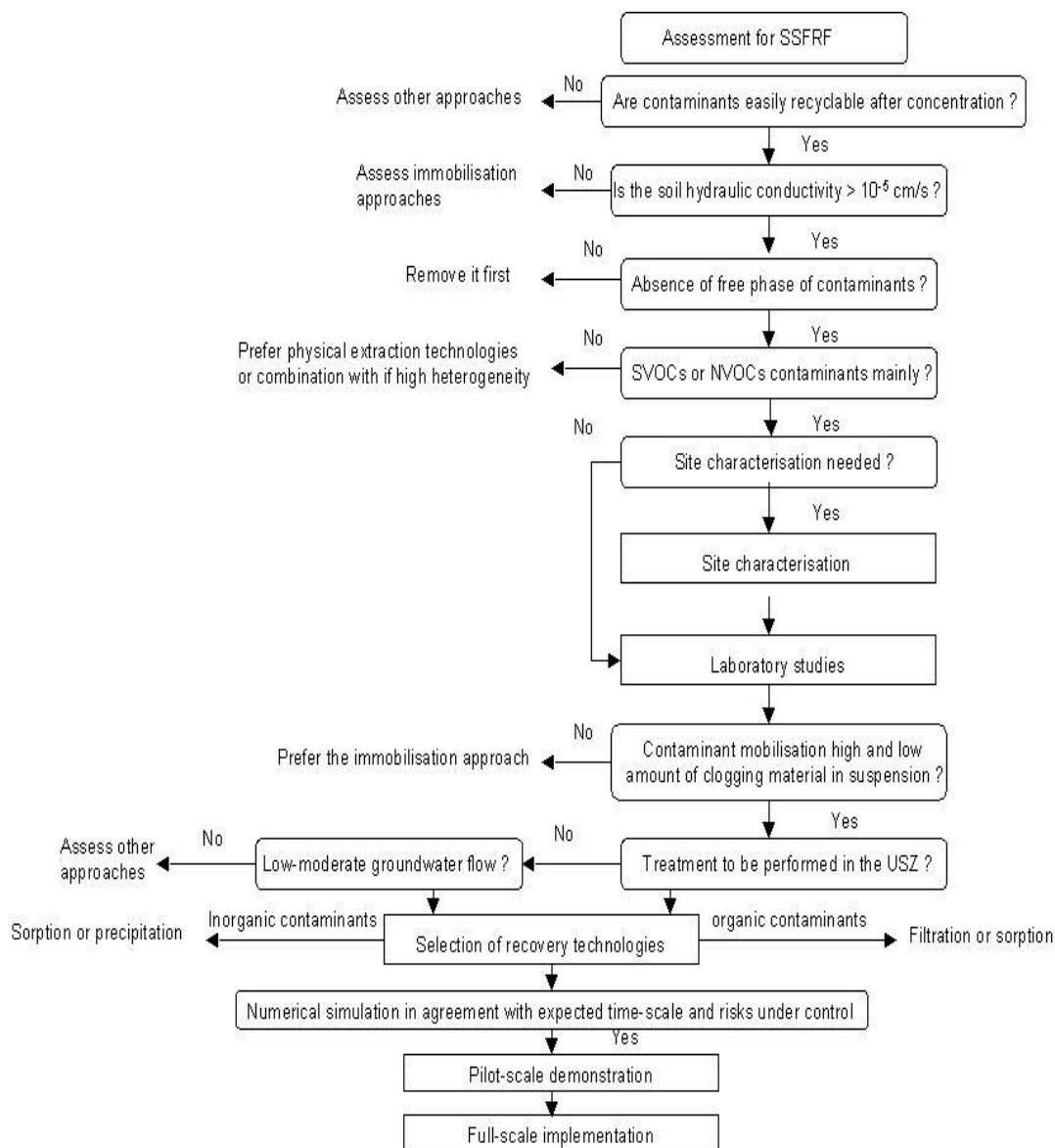


Fig 20: Flow chart for applicability of specific soil-flushing with reused fluids

Surfactants are well-known amphiphilic molecules, able to reduce the high interfacial tension between water and non-aqueous phase liquid (Paria et al. 2008). In addition, in aqueous solutions they provide hydrophobic micro-environments, named micelles, which enhance hydrophobic organic compounds solubilisation and thus their biodegradability (Cheah et al. 1998). They can enhance hydrocarbons solubility by 2-3 orders of magnitude as shown in Figure 21. For similar hydrophobic contaminants, close values for TPH in soil-leachates are often observed in lab- and field-tests, meaning fast reactions with surfactants and dissolved amount in relation with their concentration over a certain range, as long as they are accessible to the remedial fluid. However, an important technological aspect under development is the combination with air flow, as it is benefiting both for volatilisation (Mulligan and Eftekhari 2003; Couto et al. 2009), convection and porosity enhancement (US EPA 1992).

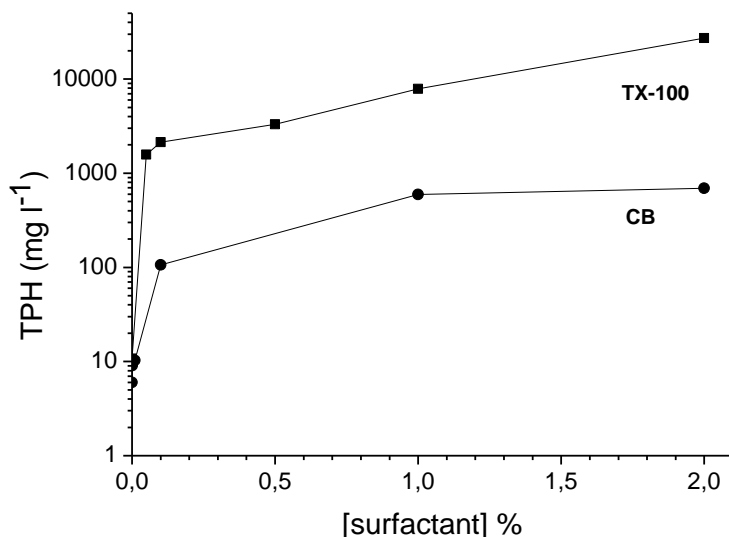


Fig. 21: TPH concentrations in soil-leachates after 2h contact time between contaminated soils from Hunedoara and surfactant solutions.

Time-scale for flushing operations can be estimated on the basis of mathematical modelling (Molson et al., 2002). Among the most important parameters (starting and targeted contaminant concentrations, radius of influence of wells, groundwater flow), the mobilisation kinetics is of main importance. This process is usually exponential as the rate-limiting steps are contaminants desorption or solubilization. At constant injection rate, it can be expressed both in terms of duration or porous volumes injected. Depending on situations (i.e. accessibility and strength of soil-contaminant interactions) rate constants may vary by orders of magnitude, as shown for example for phenanthrene (Johnson et al., 2001).

Separation technologies requested for the remediation fluid recovery for reuse need to reach high concentration factors, to be stable, robust, highly selective, cheap, safe for workers and without negative effect on the fluid properties. The specific technology to use depends strongly on contaminants and may involve a technology train (and hence additional equipment costs) if the pollution is chemically heterogeneous. Resins or precipitation (e.g. sulphur) is recommended for metals ions (Ahmed Mohamed et al., 2013, Effligenir et al., 2013), air-stripping for free volatile organic compounds (VOCs), pervaporation for those emulsified (Sabatini et al., 1998; Vane et al., 2001), ultrafiltration for emulsified SVOCs and NVOCs (Ang and Abdul, 1994), and nanofiltration for the recovery of small chemical agents.

In the following, we refer to works conducted within Timbre, where the assessment of SSFRF was carried out in extreme situations, both in terms of geology and contaminant concentrations. As mentioned in D4.4, source zones of contamination with sizes of several cubic meters at least were identified and selected on their accessibility. Selected soils were excavated and set into a cell in order to allow accurate mass balance measurements. Contaminants were more or less homogeneously distributed within the soil through excavation and filling. Contaminant concentrations and their course through treatments were measured through repeated soil sampling using systematic 3D-random selection within the cell. Total petroleum hydrocarbons (TPH C10-C40), polycyclic aromatic hydrocarbons (PAH restricted to the 16 of the priority contaminant list) and BTEX were measured by gas chromatography according to the official methods EN ISO 9377-2:2000, ISO 17993 and 18287:159 respectively. These measurements were completed by carbon oxygen demand (COD), total organic carbon content (TOC %) and metals (Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Zn) for samples from the Hunedoara test-site.

Membrane processes were used for the regeneration of treatment fluids as they were the only ones to warrant full preservation of fluids properties and so activity, while removing a substantial fraction of contaminants (95-99.9%). In membrane pressure-driven processes, a physical barrier is used to make the treatment. Depending on the size of active molecules in aqueous solutions, nanofiltration (NF) or ultrafiltrations (UF) were used to recover persulfate as an oxidizing agent or surfactants as mobilizing agents respectively. Surfactants molecules were selected on several criteria:

- 1) TPH extraction efficiency,
- 2) Low loss by sorption into soils or NAPLs,
- 3) Innocuity and biodegradability,
- 4) Ease for on-line concentration measurements with analytical field tools. Surfactant concentrations were determined by colorimetry (Rodier et al., 2005).

Measurements for the chemical oxygen demand (COD) of solutions were also carried out in order to estimate the amounts of organics pollutants in wastewater. This measurement is indicative of the presence of oxidizable organic compounds and inorganic salts.

The use of surfactant-foams instead of solutions was also more effective at the lab-scale: In mass-balance experiments, 3-4 times more TPH and PAH were shown to be removed in the gas phase with respect to the liquid phase. Surfactant-foams are meta-stable bi-phasic media made of thin liquid films and gas. The gas dispersion is obtained in surfactant solutions, liquid films being made of surfactant multi-layers and water (Singh et al. 1996).

Total Petroleum Hydrocarbon (TPH) is conventionally used to express the level of a contamination from petroleum products. The TPH is the accumulated amount of hydrocarbon compounds contained in water or soil samples, extracted with n-hexane and not absorbed on Florisil (MgO-SiO₂, obtained from Macherey-Nagel GmbH&Co. KG, Germany). TPH is a concentration of hydrocarbons having carbon numbers in the range 10-40. TPH was used as a global measurement of semi-volatile hydrocarbons including PAH.

However, in case of high fractions of highly viscous hydrocarbons like in the test zone of the Hunedoara site, a preliminary oxidation step was shown to be required to make the contaminated soil matrix accessible to surfactant solutions. Sodium persulfate, which is largely used as a soil conditioner, was selected because of security reasons and cost. The slow oxidation rate was catalysed in alkaline medium and, in addition, allowed to convert a fraction of hydrocarbons into surfactants as degradation metabolites, which could help in removing hydrocarbons too (Gryzenia et al. 2009).

3.1.2 Phytoremediation

As mentioned in detail in D4.3, phytoremediation is a technique for remediating polluted soils by use of plants (Trapp and Karlson 2001). Pollutants can both be inorganic and organic chemicals. Phytoremediation has several benefits: it is inexpensive, it seems effective, it is in situ, and it is "green" (Flathman and Lanza 1998; Schnoor et al. 1995). A special advantage of phytoremediation compared to other techniques is that soil functioning is maintained and life in soil is reactivated. A general misperception of the phytoremediation technology is thus that it is sure to remediate the site back to "normal" conditions within a reasonable timeframe, which in many cases is not true (Gerhardt et al. 2009). However, the use of phytoremediation may provide a useful tool for reaching the desired remediation goals or mitigating the environmental problems as well as functioning as a risk-reducing treatment.

Since all aspects related to phytoremediation were dealt with in D4.3, significant inserts from D4.3 are used in this comparative study!

The act of implementing phytoremediation is simple compared to other remediation technologies. Firstly, the contamination is delineated by conventional methods. Secondly, dependent on the remediation strategy and the local conditions, appropriate plant species are planted out in the area of concern. Best success is when planting in spring, when sufficient water is available for immature plants. Either before or after transplanting of plants proper monitoring of the site needs to be established to follow the remediation progress. Preferably, boreholes and installations for delineation of the polluted site can be reused for monitoring purposes. In some cases addition of nutrition may be desired in order to make the plants thrive. This depends highly on the soil properties of the site and on the remediation strategy applied. As for example for phytoextraction, where biomass is removed from the site, inhibition of plant growth may occur because of lack of nutrients. Several phytoremediation techniques have been described in Trapp and Karlson (2001), and presented in detail in D4.3: phytoextraction, rhizofiltration, phytostabilization, rhizodegradation, phytodegradation, phytovolatilization, hydraulic control, vegetation cover and buffer stripes.

Schnoor and co-workers evaluated applicability of phytoremediation (Schnoor et al., 1995, Schnoor, 1997). They found that the technique is most successful when the topsoil is polluted with chemicals being either degraded in the rhizosphere or effectively taken up by plants. For too high pollutant concentrations, toxic effects may occur, and phytoremediation therefore is restricted to lower to medium contamination levels. Thus, two key criteria for the success of phytoremediation projects is phytotoxicity (survival of plants) and biodegradability of contamination.

3.1.2.1 Decision tool

As described in D4.3, to evaluate phytoremediation feasibility and to ease the decision process, a phytoremediation flow chart has been constructed. The chart is divided into an A and a B part (Fig. 22-23). Part A concerns the applicability of phytoremediation and deals with data which have to be collected, various tests may have to be performed if no data is available in the literature, in order to make the right decisions. The knowledge obtained in part A is applied in flow chart B, which specifies the expected dominating remediation processes. The flow chart is based on earlier decision trees (ITRC 1999, Trapp 2000) and has been refined for the Timbre needs.

3.1.2.2 Data collection

Data have been collected from several projects, many of them unpublished student projects. The tests are obtained by the willow tree transpiration acute toxicity test (Trapp et al. 2000). Trees are grown in a 500 mL Erlenmayer flask and exposed to the toxin in solution. That is a kind of worst-case approach. Thus, if trees survive the conditions in this test, it may safely be assumed that they can grow outdoors on soil or groundwater polluted with a similar concentration. These measured toxicity data on trees and other plants can be used to judge the feasibility of phytoremediation projects with respect to phytotoxicity at specific sites. As can be seen, trees are generally rather insensitive organisms and can stand quite high doses of soil- and groundwater pollutants. This is of certainly an advantage for phytoremediation projects.

3.1.2.3 Mathematical modelling

The long-term fate of chemicals residing in soil (Hunedoara) or groundwater (Szprotawa) can be estimated with mathematical models that rebuild the transport and loss processes. These mass balances can also consider phytoremediation as treatment option and thus give an estimate of the feasibility, time scale and success. Typical loss processes for soil and groundwater (GW) pollutants are leaching from top soil, degradation (including biodegradation), and uptake into plants. Figure 24 (D4.3) gives a general overview of the mass balance of chemicals in soil with trees. Milestone 41 “Mathematical models to quantify biodegradation, after identification of rate-limiting processes” was within Timbre accomplished. The mathematical model was adapted to the conditions at the Timbre sites. This means both that site-specific input parameters were chosen, but also that only the relevant processes at site were considered, and that is:

- Plant uptake of heavy metals from soil at Hunedoara and
- Plant uptake of alkanes (as model compound for jet fuel) from groundwater plus biodegradation in groundwater for Szprotawa.

The models were simplified from dynamic versions to time-constant versions (i.e. no change of parameters with season, instead average annual data as input). Seen over long periods (decades to centuries), a detailed consideration of time (daily or weekly data input) is resource demanding and not relevant for the results (find details in D 4.3).

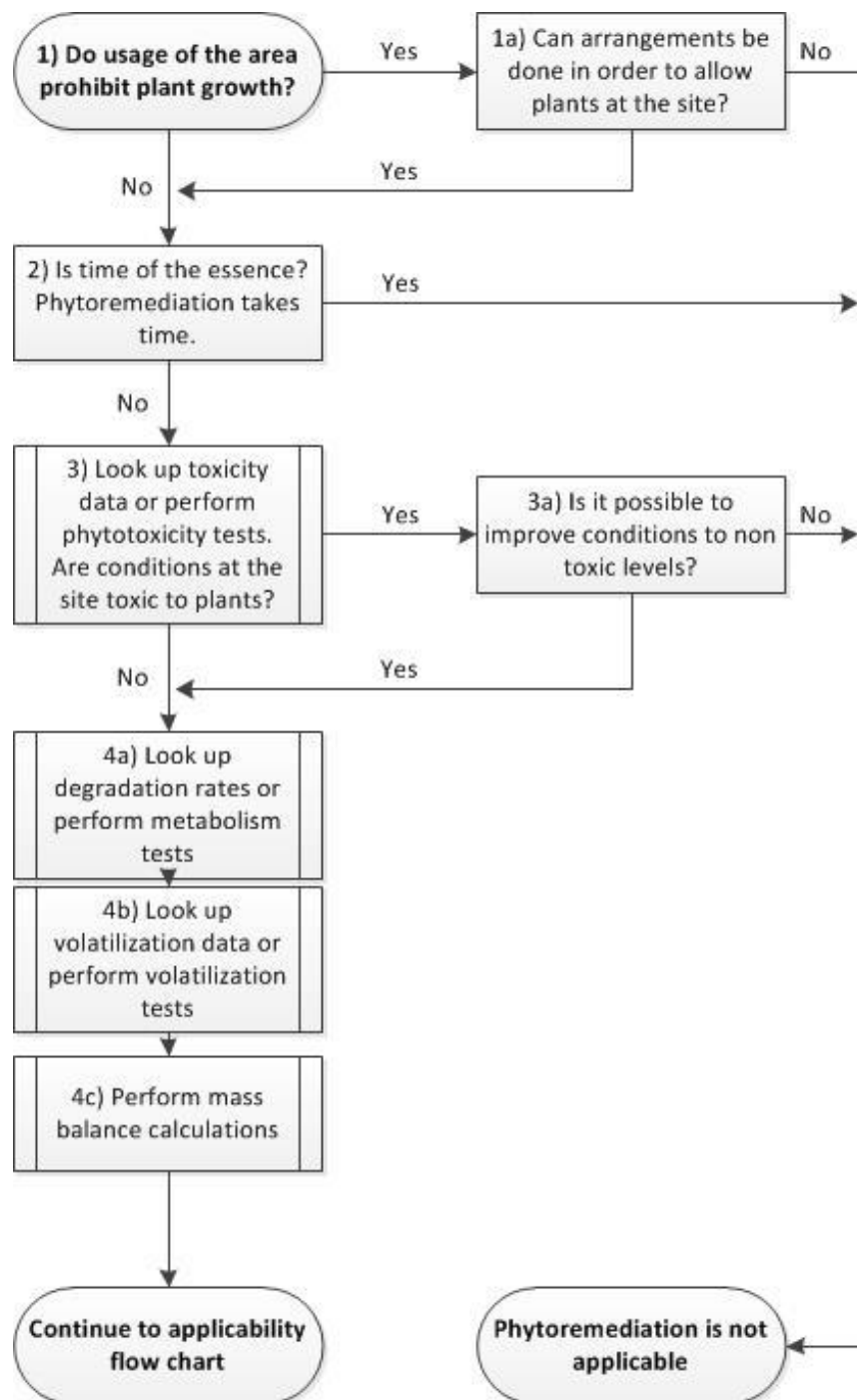


Fig. 22: Flow chart A for applicability of phytoremediation (from D 4.3)

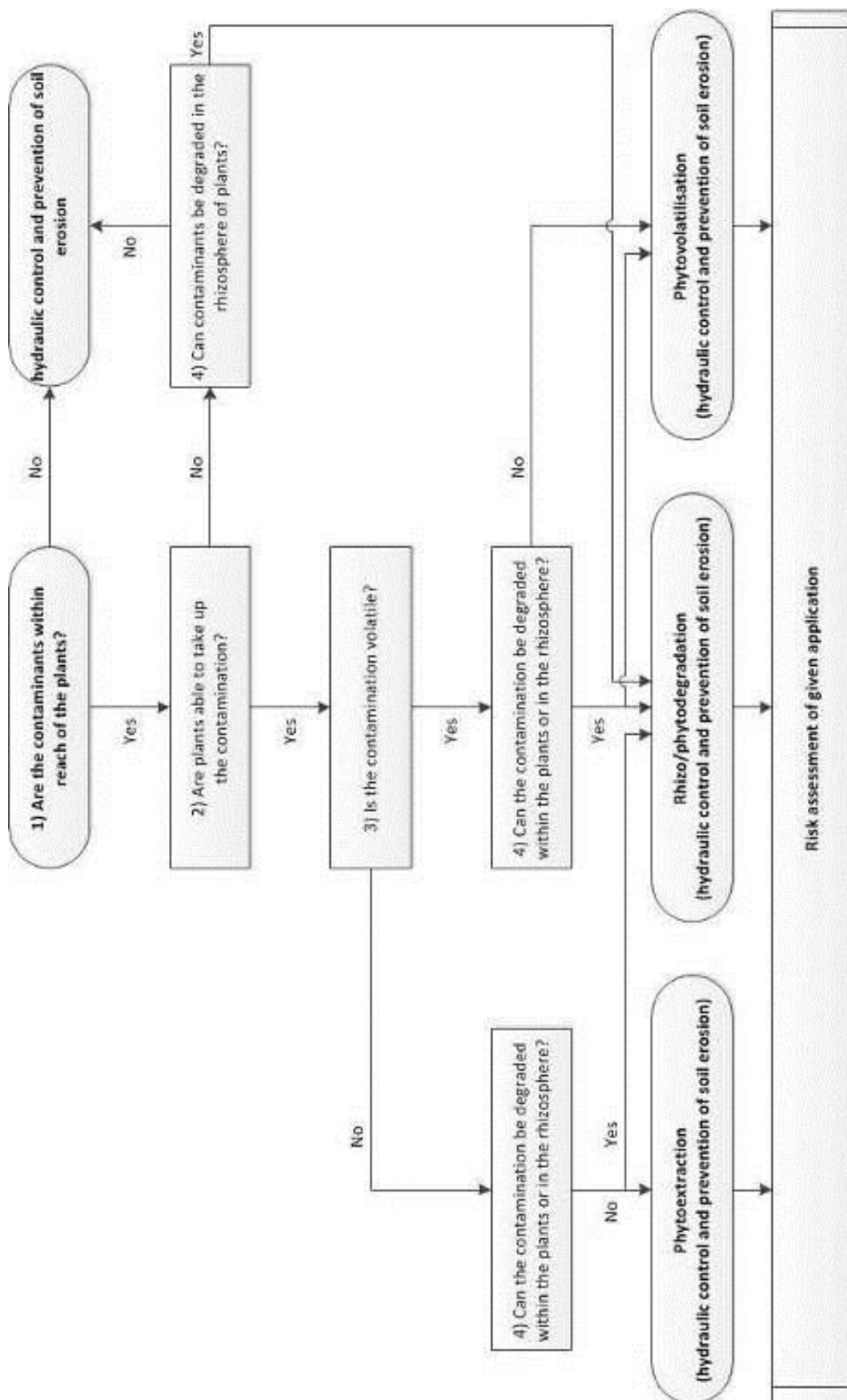


Fig. 23: Flow chart B for determination of possible (phyto)remediation processes (from D 4.3)

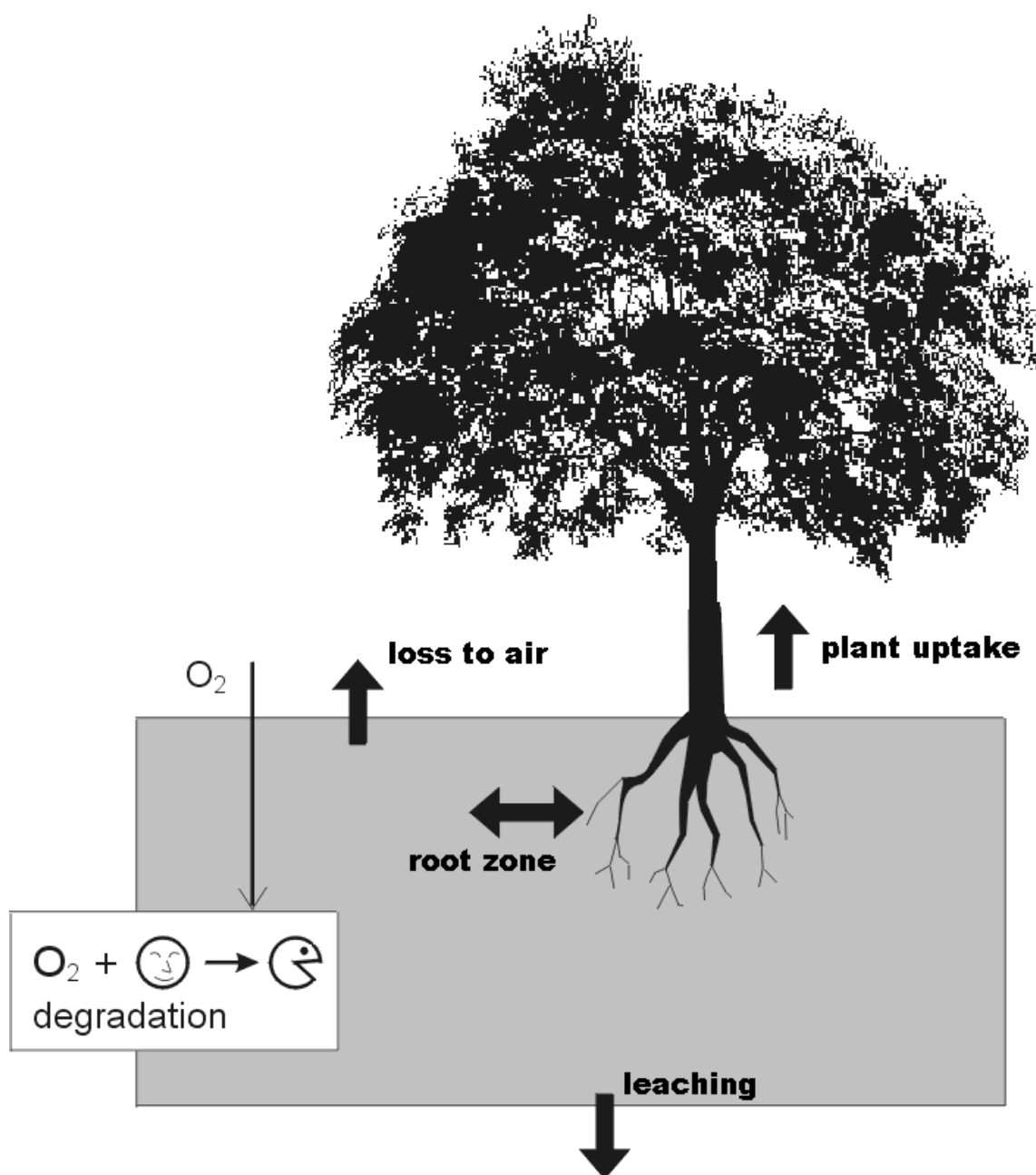


Fig. 24: Process overview for the mass balance of chemicals in soil with trees (from D4.3).

3.2 Results

3.2.1 Soil washing

The assessment of SSFRF was performed at the two Timbre test sites of Solec Kujawski (Poland) and Hunedoara (Romania).

Two preliminary campaigns carried out at Hunedoara Timbre test-site (13-14/10/2011 and 14-15/05/2013) were needed to track down suitable contaminated areas and to sample them. Finally, the area of the former wastewater station was selected to assess SSFRF, because of the challenging situation in terms of remediation. A highly viscous and hydrophobic dense non-aqueous phase liquid (DNAPL) was spreading in the underground (see red arrows in Fig. 5-right, D4.4) resulting from the spillage of phenolic tars from concrete tanks. Soil samples collected in May 2013 to set-up the treatment showed a huge hydrocarbon content (~ 40%). Because of the very low porosity of the contaminated soil and the high viscosity of hydrocarbons, a direct washing with surfactant solutions at neutral pH was unable to remove hydrocarbons efficiently. However, alkaline surfactant solutions (pH 11, carbonate buffer 1%) were 10 times more effective, because of the large amount of phenolic compounds, water soluble in their anionic form. It was decided to make an oxidative pre-treatment to increase the accessibility of surfactant solutions to the contaminated matrix and increase the efficiency for the flushing operation. Sodium persulfate was selected as oxidant, because it is among the safest oxidants available, widely used in soil amendment, cosmetics and so on. Sodium persulfate is a slow oxidant with a high redox potential (2.12 V/NHE) which requires a catalyst to be activated. In the present case, the selected catalyst was hydroxide ion as alkaline solutions were much more effective in solubilizing the organic contaminants than neutral or acid solutions.

Fortunately, the DNAPL was confined by a dense clay layer at 1.2 m depth and surrounding concrete foundations. The contaminated soil was full of DNAPL between 20 and 120 cm depth. The important amount of clay (ca. 50%) into the contaminated soil was also a challenging condition for soil-flushing both in terms of soil porosity and wastewater treatment stability.

Preliminary works to soil flushing were carried out by Timbre co-workers from the Technical University of Civil engineering of Bucharest (UTCB, Romania). The first step of remediation was, as usually agreed, to remove the pure liquid phase from the contaminated soil (remaining TOC 17.5%). In order to make a mass-balance on hydrocarbon contaminants, a nearby former Venturi channel (4.05 m-long, 1.1 m-large, and 1.7 m-depth) was used as a flushing cell for tests after it was made waterproof with cement. Five soil samples were collected before and after the oxidation step. Finally, 4 soil samples were collected at the end of the test. Contaminants concentrations and fraction of total organic carbon (TOC) in soil along the treatment steps are presented in Table 2, D4.4. Substantial removals were observed for the overall treatment (61% TOC, 62% TPH and 62% BTEX) except for PAH (15%). It is observed that the highest removal occurred during the oxidation step and that, unfortunately, persulfate was unable to oxidize PAHs, as its oxidation capacity was transferred to the carbonate radical, which has a lower standard redox potential (Bennedsen et al. 2012). During the flushing with oxidant, about 50 L of hydrocarbons were floating onto the cell surface and were recovered by skimming.

The removal of BTEX is thought to be the result of solubilisation and volatilisation. The leaching of metals was followed. Only iron and manganese were partially leachate by 27.9, and 37.5%, respectively. This removal mainly occurred during the oxidation step. None of the others metals was extracted within the experimental errors.

A strong reduction in the hydraulic constant of the soil was observed as soon as flushing with surfactant started, which was not recovered after its removal. This is probably the results of clay deposits that reduced the pores size into the soil. Despite the high fluid velocity (4 m s^{-1}) used in the UF-treatment, the presence of important amounts of stable clay and iron (6.5 mg l^{-1}) particles suspended in soil-leachates leaded to a 2.5 times reduction in membrane permeability for UF as compared to pure water, in contrast to a 1.4 factor in the case of the Solec Kujawski sandy soil. However, in each case, no pre-treatment of soil-leachates was needed before UF.

In the Solec-Kujawski test-site, surfactant based foams and solutions were used to remove TPH from the sandy soil. Field-tests were in very good agreement with lab-tests and showed that whereas the TPH concentration in leachates is limited by the surfactant concentration, their removal can mainly arise in the gas phase when foams are used. The main difficulty met with foams was their recovery at top soil surface because their viscosity. However, contaminant recovery tools as shown in Fig. 25 are feasible.

Some concluding remarks from these field tests are given below:

- Soil-flushing was able to coarsely remove 40-60% of contaminants within 3-5 weeks in two extreme situations (sandy soil moderately contaminated to highly contaminated soil with important amounts of clay). However, thresholds for reuse were not obtained, operational costs are important (workers, chemicals, energy and waste management), and workers may be exposed to hazards managing effluents despite many operations can be automated.
- Flushing with betaine surfactants solutions is poorly effective for the extraction of these hydrocarbons from tars and creosotes (1 kg removed needs 25 kg of surfactant i.e. 75 € of chemicals). However, it can be significantly improved using surfactants with ramified and phenyl-based tails (and hence much more toxic and recalcitrant) like Triton X100 (~ 40 times), foams (3-4 times because effective volatilisation) or prior oxidation (46-times). While oxidation is more effective to remove TPH (1 kg removed coarsely needs 0.5 kg of persulfate i.e. 10 € of chemicals), it was not be able to remove PAH in presence of carbonates and may need more expensive technologies and more complicated treatment of leachates. Full removal of contaminant is expected to be reached for five-time longer treatment (3-6 months).

Membranes technologies (UF, NF) are very effective for the fast recovery (within 2h) of chemicals and treatment fluids. Persulfate was completely recovered without change in pH of solutions using a single NF-step, which removed 60% of COD from leachates. UF is very effective to concentrate soil-leachates recovered from surfactant-flushing and to convert this waste (with high lower caloric value as fuel oil when it's mixed at 50%) into a product for energy-recovery. While low recovery rate were obtained for surfactant (7.5%), it can be substantially improved (5-times more) reducing their concentration for washing from 2 to 0.5% as shown in Fig. S9, but would require longer treatment (1.5-times).

Even better surfactant recovery is obtained at lower concentration, with more than 90% recovered for surfactant concentrations lower than 0.1%, despite the CMC of the zwitterionic agents used is far below ($10^{-4}\%$). In addition, despite high dilution factors, TPH-retention remained very high ($> 95\%$). Hence, dilution with groundwater is a positive aspect for surfactant recovery as long as their sorption within the soil is very low, which is the case for betaine surfactants thanks to their long hydrophilic head.

UF cannot allow environmental rejection of filtrates obtained from treatment with surfactant solutions, because the higher COD-value than the threshold limit for rejection (100 ppm). However, its combination with NF, sorption onto activated carbon or bio-treatment like treatment trains makes it possible. Finally, the high quality of treated leachates encourages their reuse, whereas high concentration factors favour the recycling of wastes. In contrast to coagulation, sorption and biological-treatments, they offer a sure treatment for reuse. In addition, while biological treatments are extensive and need a long time to be set-up (several weeks at least), membrane treatments are mobile (less than 300 kg and can be made modular) and allow an immediate reuse of treated effluents.

3.2.2 Phytoremediation

The principles, methods, data and models described in the previous chapters were used to judge the feasibility of phytoremediation at the Timbre sites Hunedoara in Romania and Szprotawa in Poland. Focus was on obstacles (phytotoxicity) and factors stimulating success (degradation). Application schemes were established. Quantitative data was collected and presented in tables. Kinetic models were established for later application at the test sites. The feasibility of phytoremediation at the Timbre sites was evaluated (see D4.3). The former steel works site Hunedoara has occasionally extremely high concentrations of toxic elements and heavy metals in top soil. At these places, phytotoxicity is likely to occur and would inhibit or distort phytoremediation efforts. Moreover, the pH at site is rather high (7.65 to 8.97), which leads to very strong sorption (K_d) of several heavy metals (in particular, nickel and lead). These high K_d values limit uptake of heavy metals, and calculated clean-up times are unrealistic (millions of years). In conclusion, phytoremediation is no option for Hunedoara. At the Polish site Szprotawa, which is a former military airport, jet fuel in >2m depth in soil and groundwater is the major pollution. The toxicity of gasoline to trees has been studied both in lab and field and is quite well known. High ROZ fuel is lethal to trees at concentrations of about 1000 mg/kg soil. Concentrations at Szprotawa are often higher (up to 11 000 mg/kg), but the peak is deep below surface (2 m depth). Thus, tree growth is possible but may be inhibited at longer periods of drought (when trees root deeper to get water supply). Vividly growing pioneer vegetation has been observed at the site, confirming this finding. Hydrocarbons are rapidly degraded under aerobic conditions, and the immediate reaction model with diffusion of oxygen as limiting factor was applied. The calculations show that jet fuel and BTEX in top soil will degrade quickly. Complete degradation under optimal conditions would occur in a bit more than a decade. Experience from real sites teaches however that hydrocarbons residing below the groundwater level will persist for longer periods, because oxygen in water has low solubility and low diffusivity. Taking all together, phytoremediation is a good option to support the naturally occurring degradation of contamination at the site, but will be slow in the high-contaminated zones.

3.3 Additional options

Additional remediation scheme are in the following chapter proposed for Szprotawa site. The concepts are based on the knowledge status gained within Timbre framework but not tested yet. Site specific pilot test are strongly recommended in order to assess the efficiency of the proposed concepts and reveal the success time horizons.

3.3.1 In-situ biological treatment with oxygen-enriched water and coupled vapour extraction: Szprotawa case

3.3.1.1 Background on the Site

Investigations of soil and groundwater contamination by jet fuels at the former Soviet airbase at Szprotawa, Poland, have been conducted during WP4 of the Timbre project. Qualitative and semi-quantitative screening methods like soil gas measurements, phytoscreening and detailed direct-push investigations by CPT and LIF were validated by selected groundwater and soil sampling.

The results have shown that the main source of contamination is situated in the former fueling area, with smaller hot spots in the vicinity of the former jet heating area and possibly along former pipelines and other subsurface structures. The main airbase fuel station area is located in the southern part of the airbase. During the soviet military operations, the fuel station consisted of 5 big tanks and smaller storage, pumping and filling facilities. The contamination was caused by free phase flow from the air base main petrol station. The area was remediated in 1997 with the use of skimmers and associated clean-up system for contaminated groundwater.

The site is located in the watershed of Bóbr and Szprotawa rivers with predominant sandy geological layers carrying an aquifer used for drinking water extraction.

Quaternary water-bearing level consists of a few water-bearing horizons with differential hydraulic connections. In the air base area quaternary water-bearing horizon is represented by 5-10m layer of sands and gravels, with hydraulic conductivity between $1,1 \times 10^{-6}$ m/s and 2×10^{-4} m/s with free water-table level (0,25-7,40 m bgl).

3.3.1.2 Background on the Pollution

During the Timbre project, the 3D-distribution of kerosene and BTEX pollution in the former fueling area has been delineated from direct-push based data, showing that the main mass of contamination is situated at relative shallow depths both in the saturated and unsaturated zone. Soil gas investigations have shown that biological degradation of the kerosene is active with the development of carbon dioxide and methane in the central fuelling area. Biological degradation is, however, hampered by relatively static groundwater conditions and consequently a lack of oxygen as a driving force.

Vapour extraction tests in the central fuelling area have shown that significant concentrations of hydrocarbons can be removed in the gaseous phase by vapour extraction.

3.3.1.3 Remediation Scenario

Taking into account the hydrogeological setting and the nature and distribution of contamination, an in-situ remediation involving bioventing and simultaneous vapour extraction is assessed as having real chances of success. The scenario envisages a series of gravel-filled trenches (6 – 12 m long) that are equipped with horizontal gas screens in the unsaturated zone (Fig. 22). The latter are used for extracting the gaseous phase of the pollution. After extraction, the gas is treated by activated carbon and then released into the atmosphere.

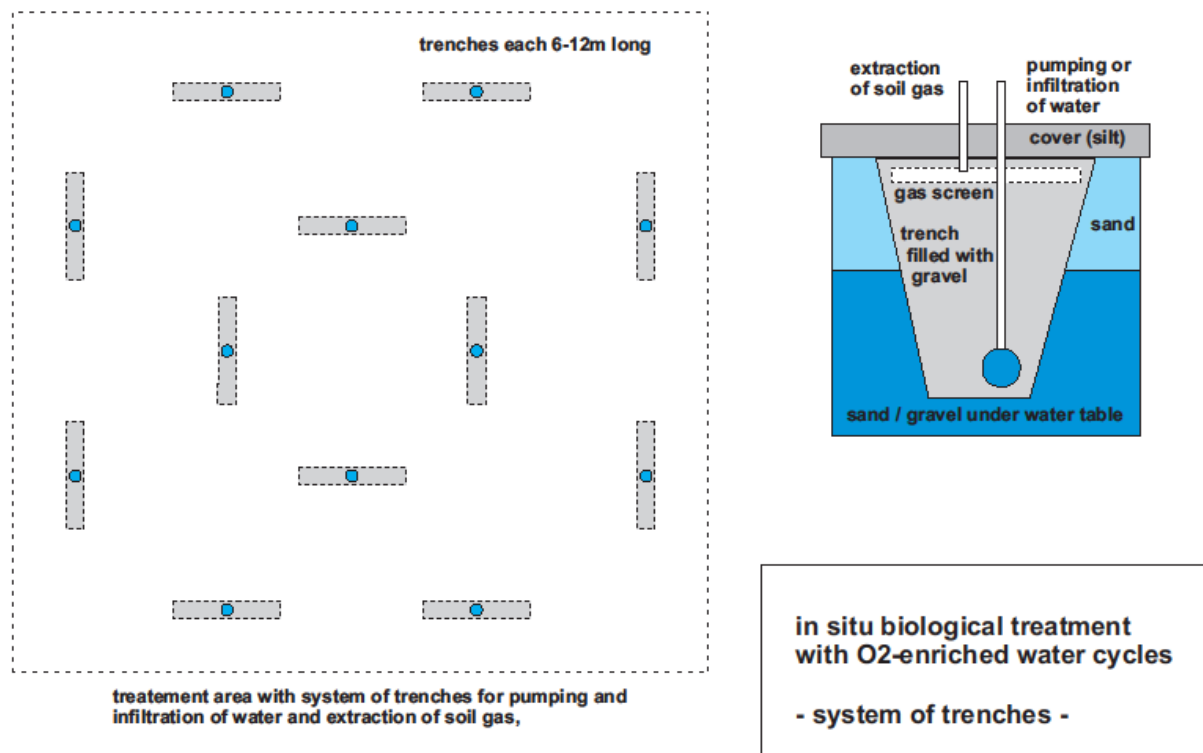


Fig. 22: In-situ biological treatment with O₂-enriched water cycles: trench system

In the saturated zone, groundwater circulation is induced by pumping and infiltration of water from and into the gravel-filled trenches (Fig. 23). The polluted water is pumped to a kerosene separation plant, where the contaminants are removed from the water. The water is then enriched with oxygen and other nutrients (N, P) and pumped back to the system, thereby supporting the natural processes of degradation.

The applicability of the process should be tested on a pilot scale in the eastern part of the fuelling area (sampling point 85A). In this area, the hydrogeological prerequisites are favorable for coupled bioventing and vapour extraction. The pilot plant should as far as possible be constructed using local resources. The gravel for backfilling the trenches could be obtained from recycling unpolluted building rubble that is present on the site (see WP5).

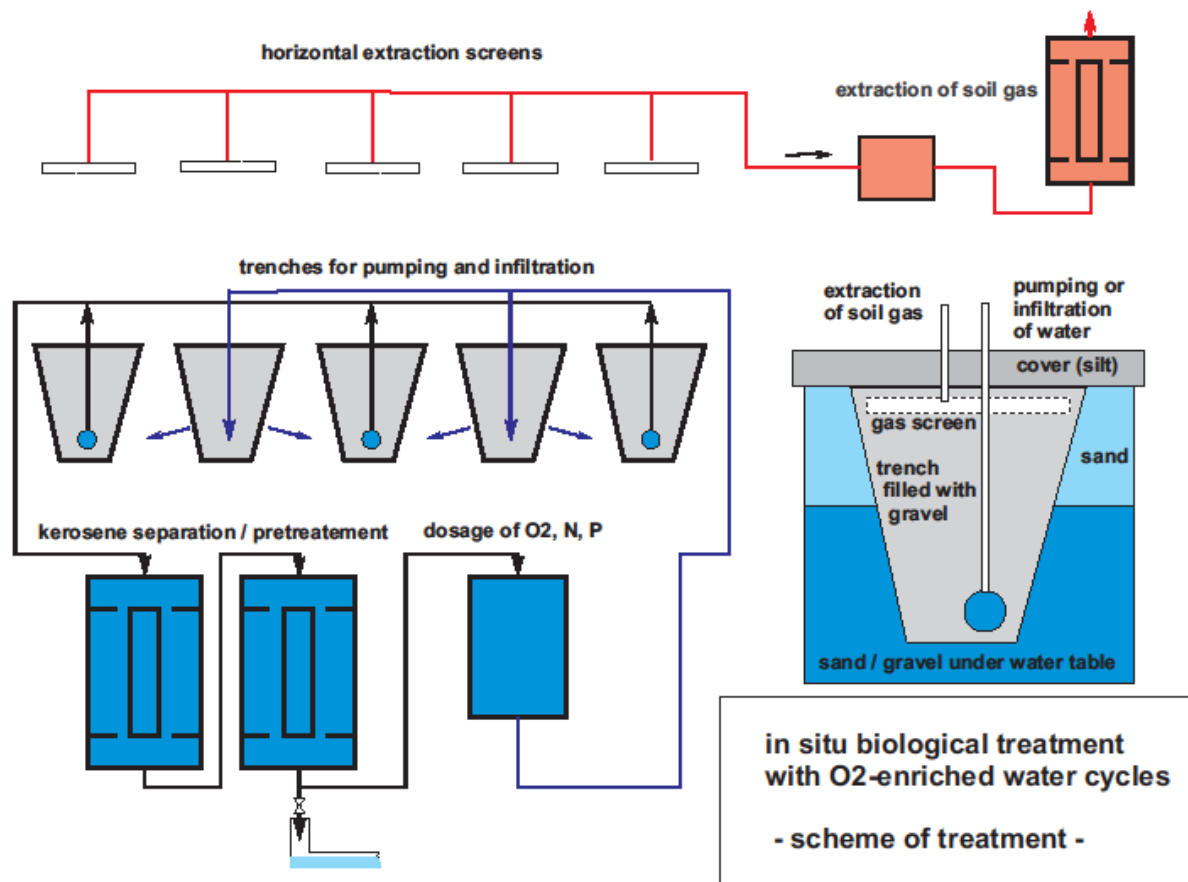


Fig 23: In-situ biological treatment with O₂-enriched water cycles: treatment scheme

3.3.2 ISCO & Biological remediation: Szprotawa case

In situ chemical oxidation (ISCO) is a cost-effective and viable remediation technology for the treatment of a wide range of organic contaminants present in subsurface environments. The method concept is based on chemical reaction between chemical oxidant and contaminants, initiated directly in *in-situ* condition by injecting the oxidant solution into the saturated zone.

This technique is efficient for elimination of most hydrocarbons, including both petroleum and chlorinated compounds. Although ISCO is a relatively mature technology for the remediation of contaminated groundwater, including source zones and plumes, on another hand it is still a developing technology due to a wide range of available oxidants and of possible variants of its application. The method has primarily been applied for treatment of chlorinated organic solvents and petroleum hydrocarbons to achieve remediation objectives ranging from reducing contaminant mass in a source zone to achieving minimum contaminant levels in a plume. To achieve more stringent remediation objectives, ISCO is almost always combined with another technology (e.g., bioremediation) or approach, e.g., monitored natural attenuation (Siegrist et al. 2011).

Besides numerous scientific results and practical applications in this field (Jain et al. 2011, Keijzer et al. 2006, Krembs et al. 2010), a premise for the application of a combined remediation approach is the positive results which were obtained by Timbre members during UPSOIL project, implemented in 2009-2012 year under the 7th European Union Framework Program. The UPSOIL (*Sustainable Soil Upgrading by Developing Cost effective, Biogeochemical Remediation Approaches*) goal was the development and implementation of innovative approach for groundwater and soil remediation; improvement of knowledge of combining chemical and biological methods - in terms of time, costs and sustainability. Laboratory tests (Sutton and Grotenhuis, 2011) proved that the most effective in-situ approach for remediation of sites contaminated with petroleum hydrocarbons is bioremediation. Even though the results of laboratory scale experiments performed for field samples were quite promising, conventional in-situ bioremediation scenario was evaluated as probably be less effective. Basic obstacles were pointed by the low oxygen concentration and the low permeability of areas affected by NAPL contamination. For in situ application, ISCO technique was recommended as supporting solution for final bioremediation boosting. The concept of coupling chemical and biological methods was applied at a site contaminated by petroleum hydrocarbons, with the focus on enhancing bioremediation through improving soil condition, raising contaminant availability for biodegradation, and easing the remediation process through improvement of hydraulic conductivity.

Based on this research (Sutton and Grotenhuis, 2011) and literature study (Keijzer et al. 2006, Siegrist et al. 2011, Wijn et al. 2010), this sort of coupled approach can be considered as applicable for Szprotawa site. For active remediation only the hot spots pointed out by the Timbre investigation activities need to be considered (mainly former gas station, Fig. 24). The approach proposed for Szprotawa case study consists of two main phases of remediation: active chemical phase and natural biodegradation. In the remediation scheme ISCO is the first step. This technique can play supporting role for final bioremediation boosting.

3.3.2.1 Phase of active remediation (ISCO)

The main aim of this stage is the removal of contaminants (kerosene, BTEX) by chemical oxidation. Taking into account the whole process of remediation, equally important element of this phase is to reverse the negative oxy-redox potential and to enhance the bioavailability of contaminants. According to the proposed remediation procedure, the key point will be to perform the chemical oxidation reactions in an appropriate manner, at the level of securing natural biodegradation potential for the further phase. Effectiveness of chemical remediation is determined by the possibilities of bringing the chemical reagent in contact with the contaminant, time of contact, redox potential of the added agent, soil oxidant demand given by local specifics of the soil and groundwater conditions (soil type, hydrogeological conditions, content of organic matter and more generally of e-donors compounds), susceptibility of the contaminants to degradation and time of degradation. Those parameters are decisive for determining the amount of applied oxidant and distribution of the injection wells. Within the ISCO scenario, datasets for Szprotawa site collected during the implementation of Timbre should be supplemented by laboratory tests conducted using various oxidants. During previous study (Sutton and Grotenhuis, 2011) high efficiency of BTEX degradation was obtained for persulfate, therefore this oxidant could be also basically recommended for Szprotawa case. The UPSOIL results are a generous basis for designing the remediation system with injection and monitoring wells and setting up the timetable of process control in Szprotawa case. The use of oxidants can have positive effects in creating good conditions for microbial development (Wijn et al. 2010). At the same time, chemical oxidation has basic negative effect with elimination of bacteria and changes of soil conditions through lowering of the pH (when persulfate is used), so ISCO phase must be carried out in an appropriate manner.

3.3.2.2 Natural biodegradation

After active remediation, soil biological potential should be sufficient to initiate natural biodegradation processes able to be stable for a longer period of time. The effectiveness depends on the availability of substrates, soil conditions and potential toxicity caused by eg. a release of heavy metals due to effects of chemical reactions. Nutrient availability and microbial growth potential (DNA tests), as well as a number of basic physical parameters valid for bioremediation (pH, redox potential, dissolved oxygen) should be monitored. For bioremediation of sites contaminated with petroleum hydrocarbons in oxidative conditions a few aspects has to be considered to secure the success of remediation:

- releasing of the contamination to water solution – desorption from soil e.g. by using surfactants,
- providing electron acceptors – developing oxidative conditions through venting the ground,
- securing availability of nutrients for microbial development.

The proposed approach relates to two important aspects of sustainable remediation: short time allowed for the redevelopment of the degraded site (investor and socio-economic perspectives), and long term rehabilitation of soil functions (ecological aspects). It provides an opportunity to link the redevelopment of degraded sites in the best business practices and to fulfill the society expectations for sustainable developments.

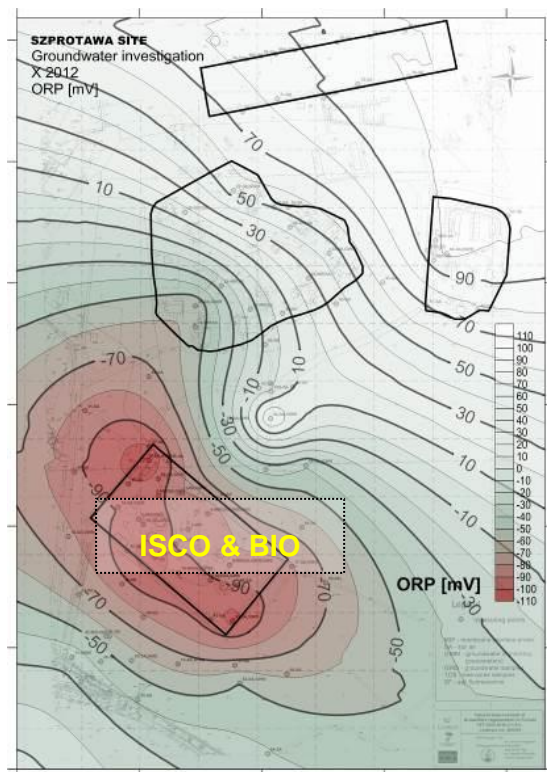


Fig. 24: Part of former air base in Szprotawa, considered for active remediation scenario (former gas station)

3.3.3 Combination of soil-flushing and air-sparging at Szprotawa site

Soil-flushing fits the situation in Szprotawa to remove rapidly the remaining hot spots as the soil is porous and groundwater flow is low. The injection of carefully selected surfactants should strongly enhance NAPL dissolution, which is the rate limiting step in the site remediation. In addition to their required physico-chemical properties, selected surfactants should be used at low concentrations (< 0.5%) and favor (or at least do not inhibit) positive microbial actions. In the special context of the Szprotawa-site the SSFRF approach is specially attractive as it may combine different technologies to improve them, such as soil-flushing and sparging, to make foams using surfactants able to stabilise air-water emulsions. The use of foams strongly improves air-sparging by increasing air viscosity by orders of magnitude (Kam et al., 2007; Farajzadeh et al., 2011). Hence, it enhances convection within the soil porous network through higher viscosity, and turbulent flows associated to the buoyancy force. Moreover, thanks to viscosity, dispersion around injection wells is better for foams than for gas or solutions (Kim et al., 2004). All these properties help for the removal of NAPLs or ganglia. Moreover, as discussed in D4.4, a major part of hydrocarbon contaminants is transferred in the gas phase of the foams especially for VOCs. Mobilized contaminants must be recovered both from the unsaturated and saturated zones as in typical sparging and flushing operations (US-EPA, 1997). Finally, this treatment would have also two others positive actions, that are the local increase in the groundwater flow and oxygen dissolution, which in that specific case are critical as discussed previously. This treatment would be set-up to remove remaining NAPLs and ganglia, after preliminary pumping operations. It should be completed doing dynamized natural attenuation with dissolved oxygen into the plume.

In that remediation scheme for the VOCs present in the Szprotawa site, the treatment for the recovered leachates involved in SSFRF would be pervaporation (Peng et al., 2003) or air stripping through hollow fiber membranes and ultrafiltration that has been shown to work nicely in a very similar situation (Sabatini et al., 1998). In that process a liquid stream containing volatile contaminants is contacted with a non-porous membrane while a vacuum or gas stream is applied on the other side. Molecules in the feed stream sorb into the membrane through their relative affinity for, then diffuse through until they reach the receiving compartment thanks to a concentration gradient. This treatment allows for the removal of VOCs from a surfactant solution without any negative effects from the foaming activity. Removal rates higher than 95% are reported, which depend both on contaminant volatility and membrane affinity, and surfactant concentration, as the latter stabilizes contaminants in the aqueous phase. It has been successfully used for the removal of TCE and other VOCs (Sabatini et al., 1998; Vane et al., 2001) like BTEX (Sabatini et al., 1998; Aliabadi et al., 2012) in leachates from soil-flushing. Contaminants are condensed from the gas phase and could be on-site recycled in energy recovery for example, as these contaminants have attractive properties for combustion engines. Positive outcomes would be volume reduction of waste to manage and cost-reduction, but they should be assessed at the pilot-scale first. A schematic representation of the proposal is shown in Figure 25.

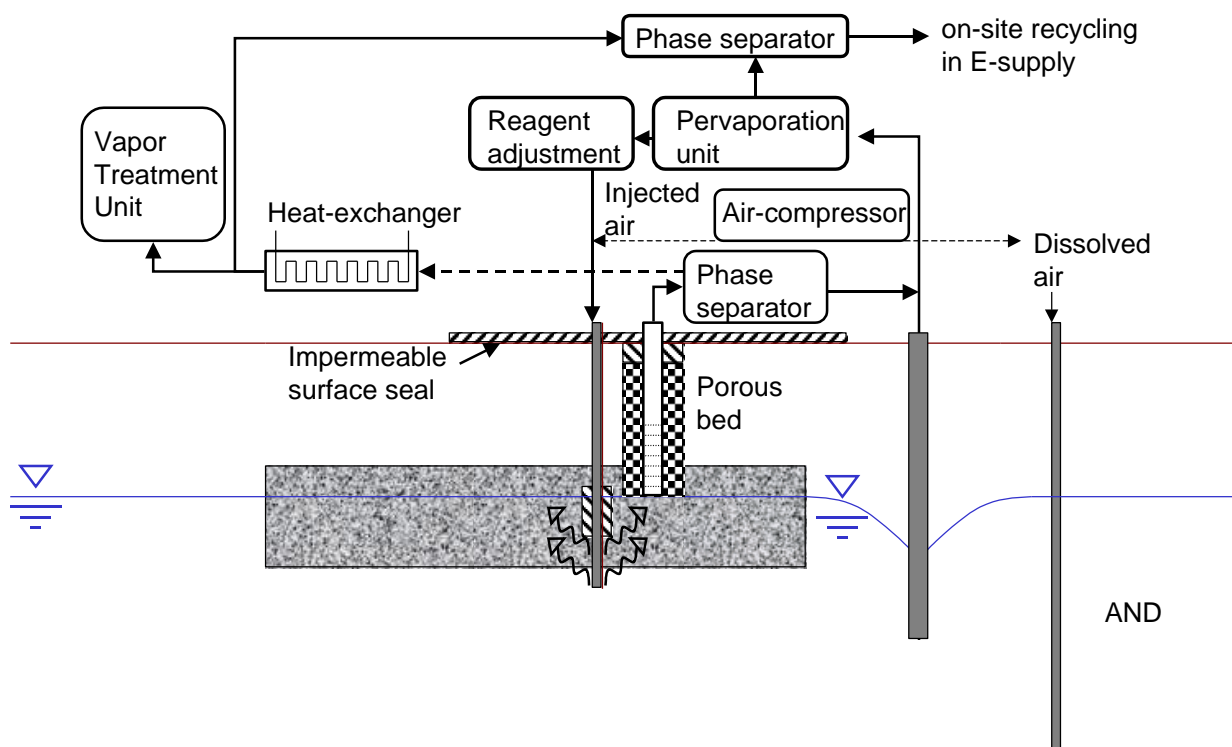


Fig. 25: Principle of the SSFRF treatment proposed for the Szprotawa airbase. A coarse prefiltration unit (50 μm) has been omitted before pervaporation for clarity.

4. Comparative evaluation of advantages and uncertainties

4.1 Investigation

Tree coring is an investigation method which enables a rapid screening of the site no matters the size. Even large (megsites) sites are being dealt with in reasonable time and cost horizons. The prerequisite is the presence of adequate tree species, distributed more or less even over the whole site surface. Despite the fact, that the method doesn't produce concentrations able to be compared to other investigation methods, the semiquantitative scale is able though to structure and rank the site in terms of contaminant distribution. Favorable or disadvantageous factors enable or disable the rather integrative capacity of the trees to point out the underground contaminant level.

Soil gas is a shallow investigation method which yields shortly reliable results in terms of spatial distribution of volatile contaminants. Since the method has a significant integrative characteristic, the uncertainty related to the detection capacity is relatively low. The method is restricted to volatile compounds, lithology and hydraulic parameters play a key role in emphasizing respectively restricting its strength.

Direct Push based investigation methods (MIP, LIF, HPT, etc.) point out a major advantage by being able to reliably provide high resolution signals over the screened intervals. Being a point methodology, 3D models of the underground in terms of lithology, hydraulics and contamination can be easily buildup based on the high resolution vertical profiles. Almost all DP-high resolution investigation methods provide indirect measurements in a real time frame, allowing therefore quick and efficient on-site decisions. To calibrate the measured signals and validate their findings, depth oriented or integral sampling (soil, soil gas, groundwater) may provide the 100% quantitative feature of the site characterization procedure.

Leaching tests provide a quick and cheap assessment for the risks of waterborne transport of pollutants associated to the contaminated field. They help for decisions about strategies to set-up with respect to the control of contaminants and the selection of treatments in term of immobilization, mobilization or degradation, if any is needed. Usually they provide coarse characteristics of the site as composite sampling is often done to minimize costs, and results are depending on the sampling plan quality. However, as soon as hot spots are identified, the method provides coarse estimation for contaminant flow and allows anticipating the behavior during and after the remedial step.

Timbre has proved that a combined investigation strategy involving the use of the above mentioned methodologies has major chances of success: tree coring for a quick coverage of the site followed by shallow soil gas and Direct Push based profiling on target areas.

4.2 Remediation

SSFRF was set-up and assessed for soils contaminated with divalent metals and petroleum hydrocarbons from creosotes and phenolic tars, as it especially fits them. However, due to the characteristics of available contaminated sites, field assessments focused only onto hydrocarbon related contaminants (TPH, PAH, BTEX). As long as the soil hydraulic conductivity was higher than $10^{-3} \text{ cm s}^{-1}$ and contamination levels $< 20\%$, it was observed that SSFRF was able to fit the situations. Results showed that despite innocuous betaine surfactants solutions are poorly efficient in removing hydrocarbons, the use of surfactants foams or oxidation may improve the process significantly. The inability for activated persulfate to oxidize PAH was only the result of carbonates that reduced the available oxidation potential. An easily transportable filtration unit was built and assessed into the field. This assessment showed that UF and NF-treatments of soil-leachates strongly favor the reuse of washing fluids and chemicals, and the recycling of liquid wastes into the energy recovery and environmental rejection of NF-filtrate. In addition, they offer stable treatments and reduced operation costs and use of chemicals, but surfactant concentrations in leachates should be lower than 0.1% for their significant recovery.

Finally, membranes technologies specially fit the following situations:

- Flushing or washing treatments of hydrocarbon contaminated soils using persulfate like oxidant or surfactants,
- rough fields with low operating space,
- pressure onto the use of water resources,
- low to moderate wastewater volumes to treat ($< 10 \text{ m}^3 \text{ day}^{-1}$)

Cross-filtration with high flow velocity allowed to get stable treatment despite the presence of clogging material in suspension like clay or iron(III). Considering costs assessment from field-tests, benefits balance operating treatment costs mainly through the substantial reduction of liquid wastes. Balance on membrane costs is expected in 1-year. However a look on the overall costs show that investment costs for water treatment (20-50 k€ for $5\text{-}10 \text{ m}^3 \text{ day}^{-1}$) are about 20 times higher than costs for chemicals. Hence, cheaper separation technologies should be used for the full development of this approach.

Phytoremediation. When the phytoremediation technology arose, the expectancies were high as research seemed promising. However, non-satisfactory field applications have often been reported (Gerhardt, 2009), leaving the phytoremediation technology with a less positive reputation. Despite of this, phytoremediation still has potential as a useful remediation method, especially when combined with other methods which handle high concentration areas (where phytotoxicity may occur), e.g. source removal. It is crucial to emphasize the importance of site and contaminant characteristics and to gather as much data as possible, data concerning physical chemical properties, total mass, toxicity and degradability of the pollution present, in order to assess realistic remediation time horizons. The predominant limitation of phytoremediation seems to be the long, sometimes extremely long, remediation time frame. Especially phytoextraction of heavy metals takes long time (thousands of years, predicted) and does not provide a final solution because the heavy metals reside in wood or even cycle between top soil and leaves or spread in the ecosystem. However, heavy metals cannot be destroyed, and there is no real treatment for them except making them non-available. This means dumping in deep holes, or fixation in glass or street sublayers. The volume of dump material can of course be reduced by methods such as soil washing or soil electrics, or burning of organic matter, but heavy metals as such will never be destroyed by these methods. On the other hand, there is no need for a site clean-up when the site is used for forestry purposes only - unless another good needs to be protected, such as groundwater. Allowing tree stands over centuries does not cost any maintenance and will, in most cases, be the cheapest alternative versus clean-up of any kind.

Contrary, in urban areas, where the site is to be used soon again, and where soil (or better: area) has a high value, a slow and long-lasting treatment method such as phytoremediation will not be a competitive treatment method. Alone the time frame will in many cases completely rule out phytoremediation. Unfortunately, most if not all (Western) cities that are older than 100 years have heavily polluted top soils. The reasons are heating with coal fires, traffic with leaded fuel and the non-existence of any rules for industrial production and waste before the late 1960ies.

In Denmark, phytoremediation has been tested on several sites, and the results were considered as disappointing. From a scientific perspective, this is due to unrealistic expectations, or at least ill-designed projects. Some examples, we have investigated the Valby sludge basin (Algreen et al. 2013, D 4.2). There, a >5 m layer of heavy polluted sludge (organic and inorganic) was planted with willows and trees. Due to methane production, rooting depth rarely exceeds 1 m, and plants suffered the first years, many died. After ten years, the content of some pollutants was measured again (Algreen et al. 2013, D 4.2), and no significant difference to the initial levels was found. We do not know what the engineers carrying out the project had expected. But it seems, from a scientific perspective, rather clear that a 5 m layer of anoxic toxic waste does not get valuable soil within a few years just by planting trees on top. Another well-investigated site is a former gas works, the Holte midpoint (Trapp and Christiansen 2003). There, cyanide is present as Prussian blue, which forms solid blue particles. In a first cleaning attempt, an engineering company tried to remove the cyanide substrate by excavation. Later investigations showed that more than expected substrate remained. Poplar trees were planted in the year 1999/2000 and grew very good at the site. The site owner (the local municipality) was disappointed that cyanide (Prussian blue) was still present after ten years. Our scientific analysis showed that cyanide is very well

degraded both as free cyanide (HCN and the anion) and as simple iron cyanide (ferro- and ferricyanide) (Trapp and Christiansen 2003, Larsen et al. 2005, Larsen and Trapp 2006), but the time-limiting factor for the cyanide removal is the dissolution kinetics of Prussian blue (ferroferricyanide). Prussian blue is a solid that can of course neither be taken up by plants nor be attacked by bacteria. The dissolution depends mostly on pH and would have taken about 1000 years. This was known at the time of planting the trees. During dissolution, all free cyanide and all soluble iron cyanide in reach of the plants is rapidly degraded, making phytoremediation a protection measure against mobile cyanide. This effect is of course highly desired. But plants cannot be a treatment method for solid cyanide. After ten years, the treatment was considered a failure, but this is due to ignorance of these well-known scientific facts. Disappointment about phytoremediation can thus be partly explained by expectations of miracles and by naive hopes (or promises) of those ignoring the biological, chemical and physical principles.

The slow uptake of heavy metals into plants bears also a chance: “phytoexclusion” means the use of plants, non-food crops or also strains of agricultural crops which do not take up (or very little) heavy metals (Dickinson et al. 2009). These plants can then be used even on soils with pollution above quality standards to produce biofuel or food. A popular and wide-spread example where this concept is helpful is “Urban Gardening” - all over the world, the population in the mega cities starts to grow their own food, not only in developing countries, but also in rich Western cities such as New York or Copenhagen.

A major strength of phytoremediation is the applicability at huge size areas and the self-sufficiency. The implementation costs are fairly inexpensive, and may be compensated by harvest products. After implementation the main expenses are connected to monitoring of the site, if this is required. The monitoring costs equal those of (monitored) natural attenuation MNA. From that perspective, phytoremediation combined with the production of biofuel or wood, is the treatment of choice wherever a fast removal of pollution is not feasible, or not necessary, where a reuse of the area is not expected within a lifetime, and where the sheer size of the area makes all other treatment efforts far too expensive. There are many of such sites, among them:

- the remote mega-sites stemming from former mining activities
- brown coal and black coal heaps
- old waste sites and larger sludge disposal sites.
- abandoned military areas (e.g., Szprotawa)
- diffusively contaminated abandoned brownfields in non-urban areas.

There are plenty of those sites in Europe. Also "wild" phytoremediation is helpful, which means the development of the climax vegetation on an undisturbed site.

Phytoremediation is a feasible option at Szprotawa and will support the natural attenuation of the fuel products. The prognosis is that within one or few decades, jet fuel will vanish from top and deeper aerated soil (vadose zone), while rests and lenses of hydrocarbon will remain for much longer (several decades) in groundwater, but with shrinking extension.

The cost of phytoremediation greatly depends on monitoring activities, that are required by authorities for any natural attenuation project. We will here only list the extra costs that appear due to the trees. In addition to the monitoring, additional expenses are expected due to planting of trees, for weeding, initial watering, maintaining and (in case of drought or other calamities that lead to loss of many trees) replanting. Often willows and poplar are preferred to other tree species due to their high transpiration and fast growth (D4.2). Moreover, these species can be provided - and planted - as cuttings, which reduces the costs quite significantly. The costs per cutting can be down to $< 1/2$ € (Ny Vraa, 2013) and planting done by unlearned labour can be done for $< 10\,000$ €/ha (this depends, of course, on the minimum fee in the respective country). In forestry it is common to plant initially denser, 4 to 8 trees per m^2 . If 1 cutting is needed per m^2 the price for 1 ha is approx. 20 000 to 40 000 Euro costs for the trees. Alternatively, the usually upcoming natural pioneer vegetation can be supported, with much less costs, but slower appearance of a forest. Doing phytoextraction with trees allows harvesting of wood. Disposal is not necessary when treating degradable and volatile contamination and the wood can perfectly be used and sold on the market. It is common to use the wood from such sites as biofuel (e.g., for pellets production, or for fire wood). Residuals of jet fuel would not damage such use but even lead to better material.

4.3 Short exemplary evaluation of remediation options for Szprotawa site

Szprotawa site is a case with relatively low risks of further migration of contaminants in the groundwater and low risk for human. Selection of the remedial approach depends on the redevelopment scenario planned for the site. The following approaches can be taken into account:

- Quick remediation based on ex –situ methods,
- Short term remediation
- Long term remediation
- Suspended usage

The short evaluation of the approaches is presented in Table 5. The analyzed approaches differ with regard to time, costs and sustainability (low environmental burden). The most balanced is the soil vapour extraction or bioventing being positively evaluated in all aspects.

Table 5: Short exemplary evaluation of remediation options for Szprotawa site

Approach	Considered technologies	Criteria of evaluation		
		time	costs	sustainability
Quick remediation (based on <i>ex-situ</i> techniques)	Polluted soil replacement, eventual <i>on-site</i> soil remediation. Supporting techniques could be needed (ISCO)	+++	---	---
SHORT-term remediation	ISCO based techniques	-++	--+	--+
LONG-term remediation	Bioremediation combined with ISCO techniques, enhanced bioremediation.	--+	--+	-++
	Soil vapour extraction, and/or bioventing	-++	-++	+++
	Phytoremediation supported by humification, lime treatment (land farming)	---	+++	+++
Suspended usage	MNA, phytoremediation/ forestation, continuous risk control	---	+++	+++

Based on the spatial characterization of the contamination, specific areas might be appropriate for specific remedial approaches:

- the former fuel base with BTEX contamination at the level of 150 - 240 mg/kg of d.m. and benzines 1100 - 4700 mg/kg d. m. respectively the engine heating area with BTEX being at the level of 50 - 80 mg/kg of d.m. and benzines 9000 - 11000 mg/kg d. m. for which all approaches can be considered, depending on the plans of future use,
- the remaining areas with contamination of BTEX at the level of 2,3 mg/kg d.m. and benzines 23 mg/kg d. m. for which natural attenuation and risk control are sufficient remedial measures taking into account current land use – forest and green area.

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Annex I: Contributors to the report and Disclaimer

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